Materials Science
Lecture #2

Atomic Structure
and
Interatomic Bonding

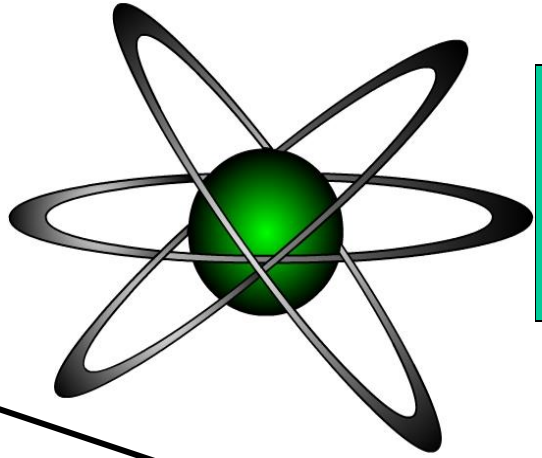
ISSUES TO ADDRESS...

- What promotes bonding?
- What types of bonds are there?
- What properties are inferred from bonding?

Structure of Atoms

ATOM

Basic Unit of an Element
Diameter : 10^{-10} m.
Neutrally Charged



Nucleus

Diameter : 10^{-14} m
Accounts for almost all mass
Positive Charge

Electron Cloud

Mass : 9.109×10^{-28} g
Charge : -1.602×10^{-9} C
Accounts for all volume

Proton

Mass : 1.673×10^{-24} g
Charge : 1.602×10^{-19} C

Neutron

Mass : 1.675×10^{-24} g
Neutral Charge

QUARKS??

https://www.fizzics.org/quarks-and-leptons-notes-and-video/

Atomic Structure (Freshman Chemistry)

- atom – electrons – 9.11×10^{-31} kg
  protons, neutrons } 1.67×10^{-27} kg

- atomic number = # of protons in nucleus of atom
  = # of electrons of neutral species

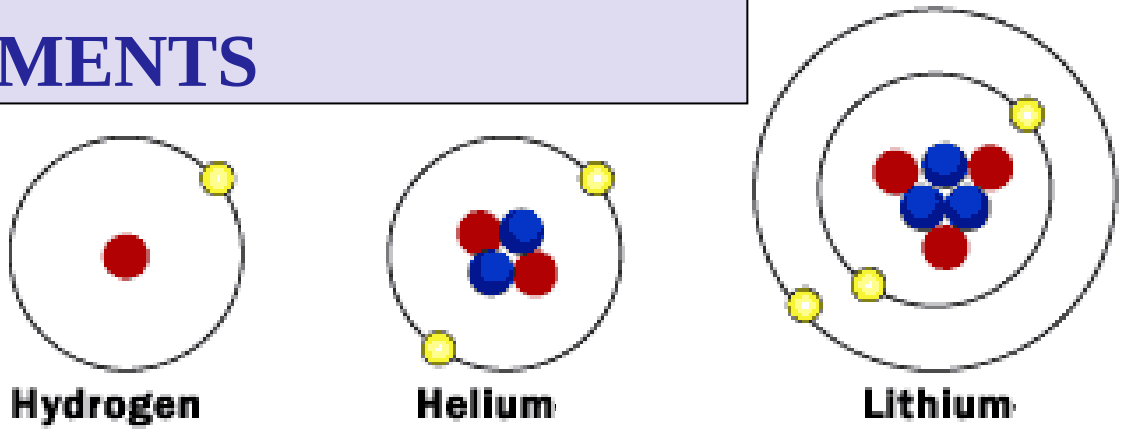
- A [=] atomic mass unit = amu = 1/12 mass of ^{12}C

Atomic wt = wt of 6.023×10^{23} molecules or atoms

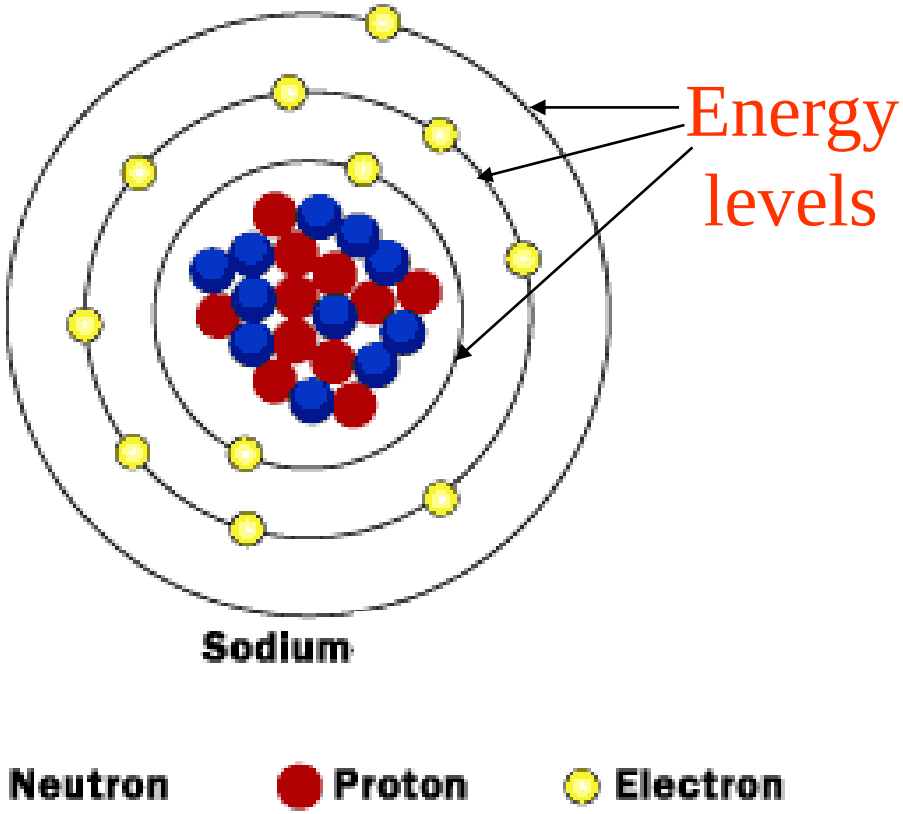
1 amu/atom = 1g/mol

C 12.011
H 1.008 etc.

ELECTRONIC STRUCTURE OF ELEMENTS

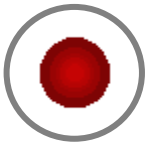


Electrons of an atom can have only very distinct energy values. Therefore, the electrons are restricted to specific “energy levels” or “stationary states”

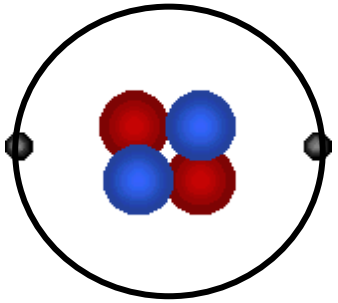


Electrons in these energy levels rotate about the nucleus in fixed orbits, without radiating or absorbing any energy

H atom



He atom



Electron Structure of Atoms

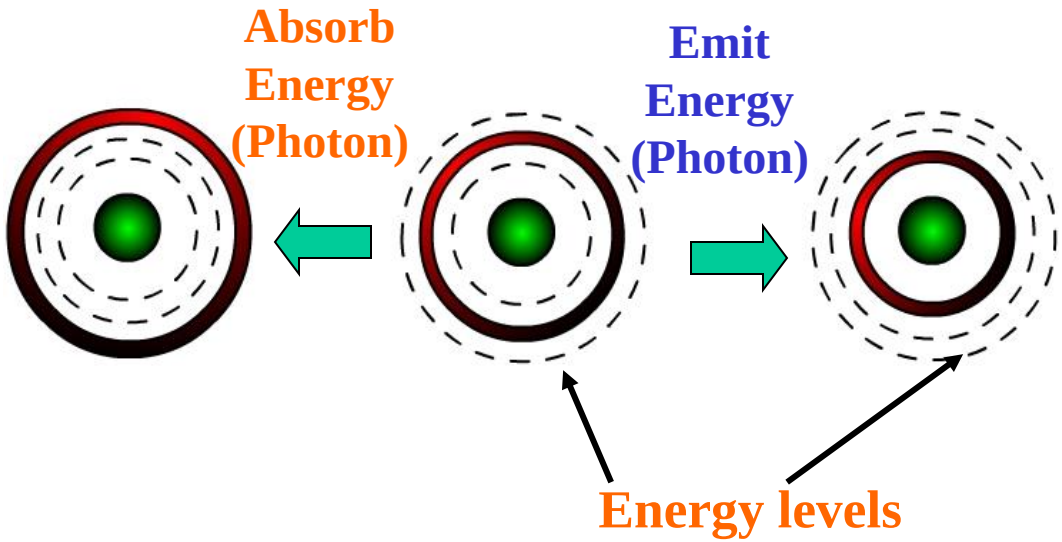
- **Electron rotates at definite energy levels.**
- **Energy is absorbed to move to higher energy level.**
- **Energy is emitted during transition to lower level.**
- **Energy change due to transition = ΔE =** $\frac{hc}{\lambda}$

h=Planks Constant

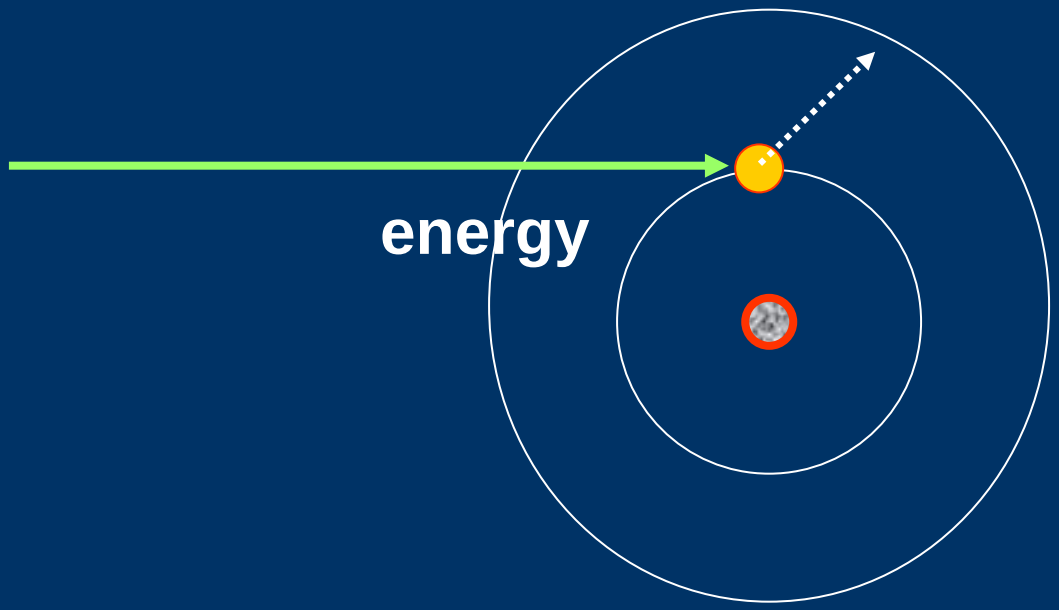
$= 6.63 \times 10^{-34}$ J.s

c= Speed of light

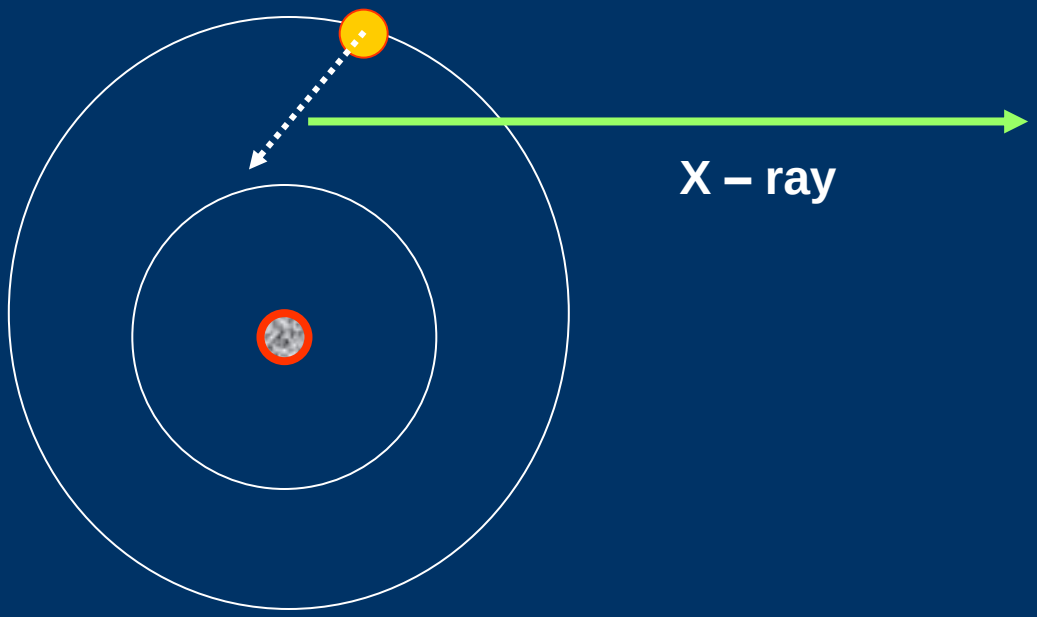
λ = Wavelength of light



When an electron receives energy it moves from a lower to a higher energy level



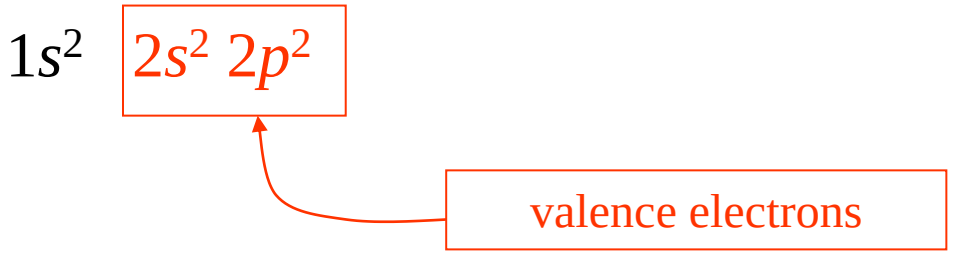
Movement of the electrons from a higher level to a lower level of energy results in emission of radiant energy (electromagnetic radiation)



Electron Configurations

- Valence electrons – those in unfilled shells
- Filled shells more stable
- Valence electrons are most available for bonding and tend to control the **chemical properties**

  – example: C (atomic number = 6)



Atomic Structure vs Properties

- Valence electrons determine all of the following properties

1) Chemical
2) Electrical
3) Thermal
4) Optical

SURVEY OF ELEMENTS

- Most elements: Electron configuration not stable.

Element	Atomic #	Electron configuration	
Hydrogen	1	$1s^1$	
Helium	2	$1s^2$	(stable)
Lithium	3	$1s^2 2s^1$	
Beryllium	4	$1s^2 2s^2$	
Boron	5	$1s^2 2s^2 2p^1$	
Carbon	6	$1s^2 2s^2 2p^2$	
...		...	
Neon	10	$1s^2 2s^2 2p^6$	(stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$	
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	
...		...	
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	(stable)
...	...	...	
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$	(stable)

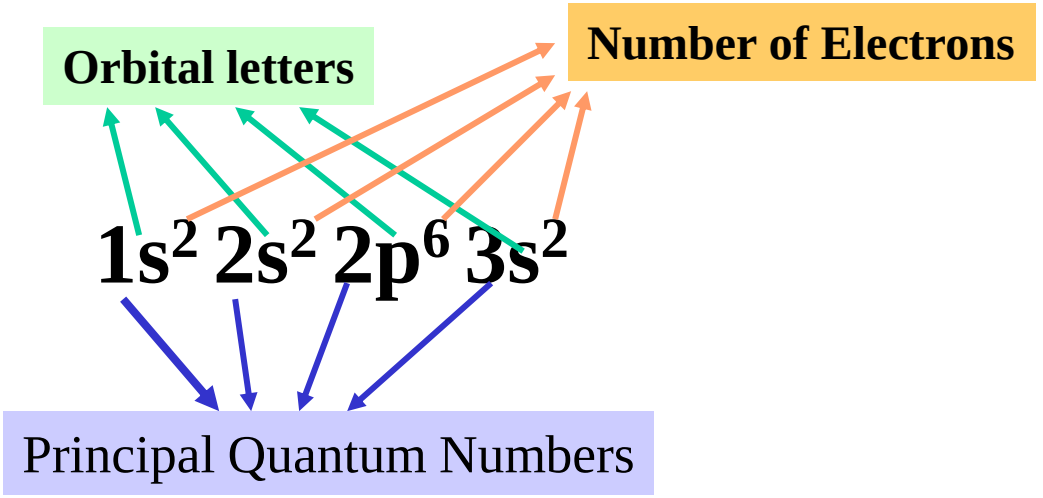
Adapted from Table 2.2, *Callister 7e.*

- Why? Valence (outer) shell usually not filled completely.

Electron Structure of Multielectron Atom

- **Maximum number of electrons in each atomic shell is given by $2n^2$.**
- **Atomic size (radius) increases with addition of shells.**
- **Electron Configuration lists the arrangement of electrons in orbitals.**

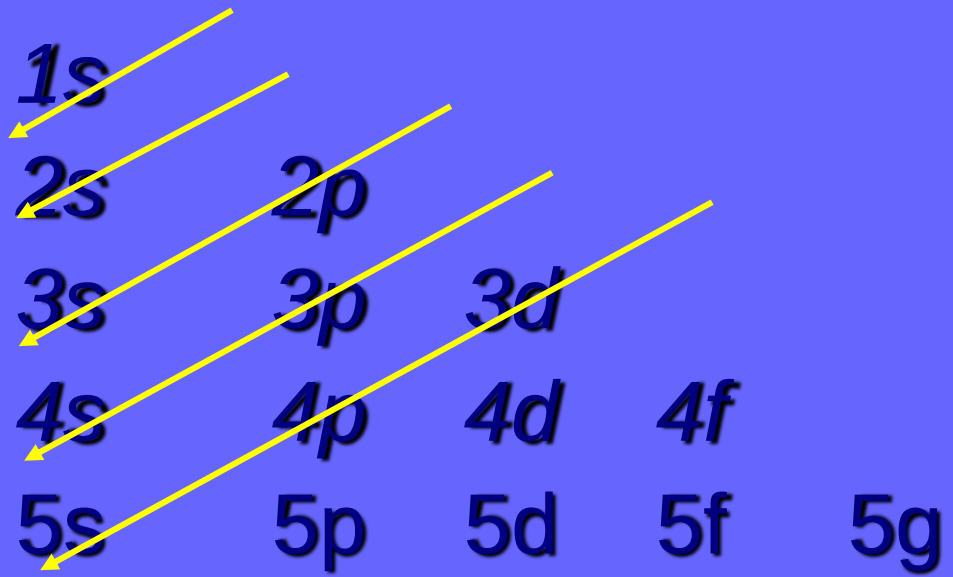
➢ **Example :-**



➢ **For Iron, (Z=26), Electronic configuration is**

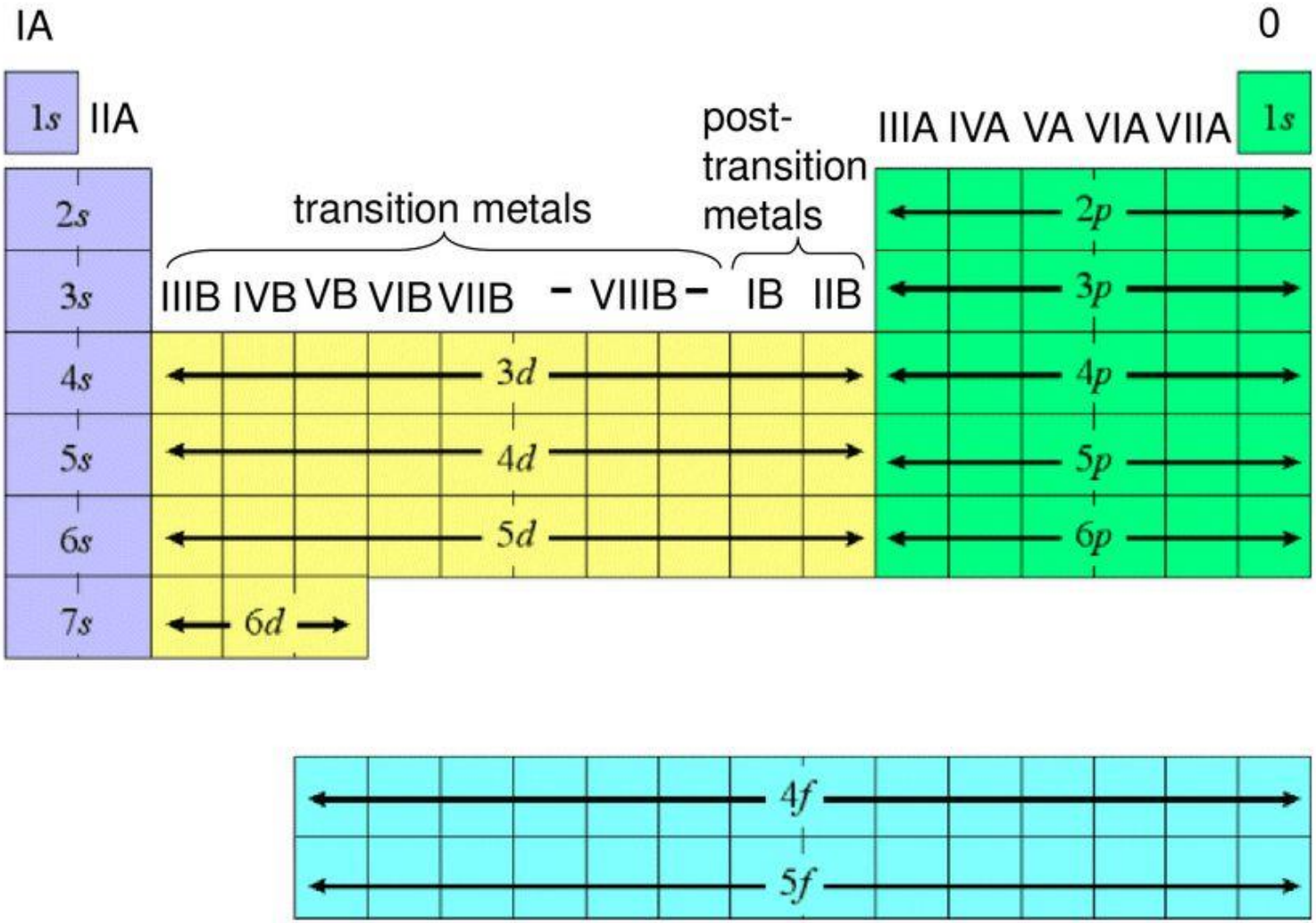
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

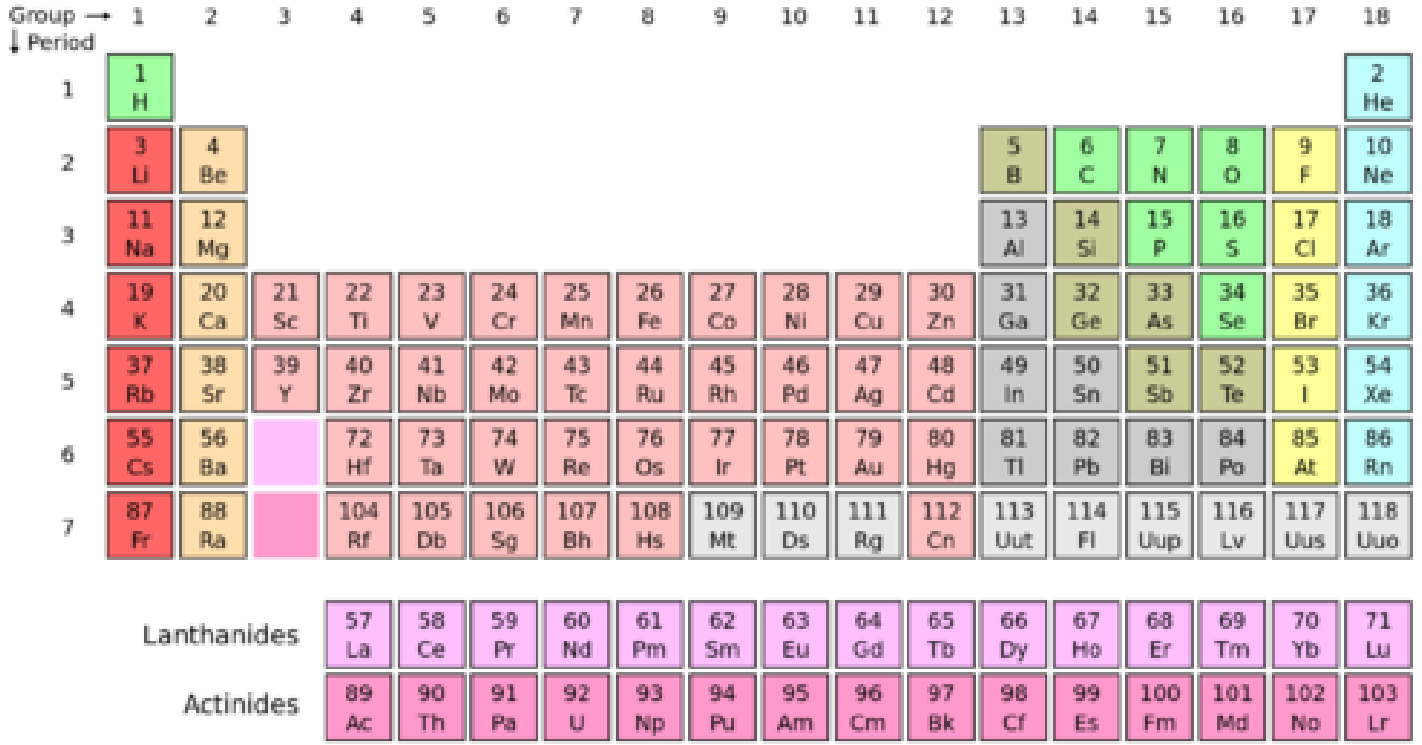
Sub-levels with the lowest energy are filled before those with higher energy



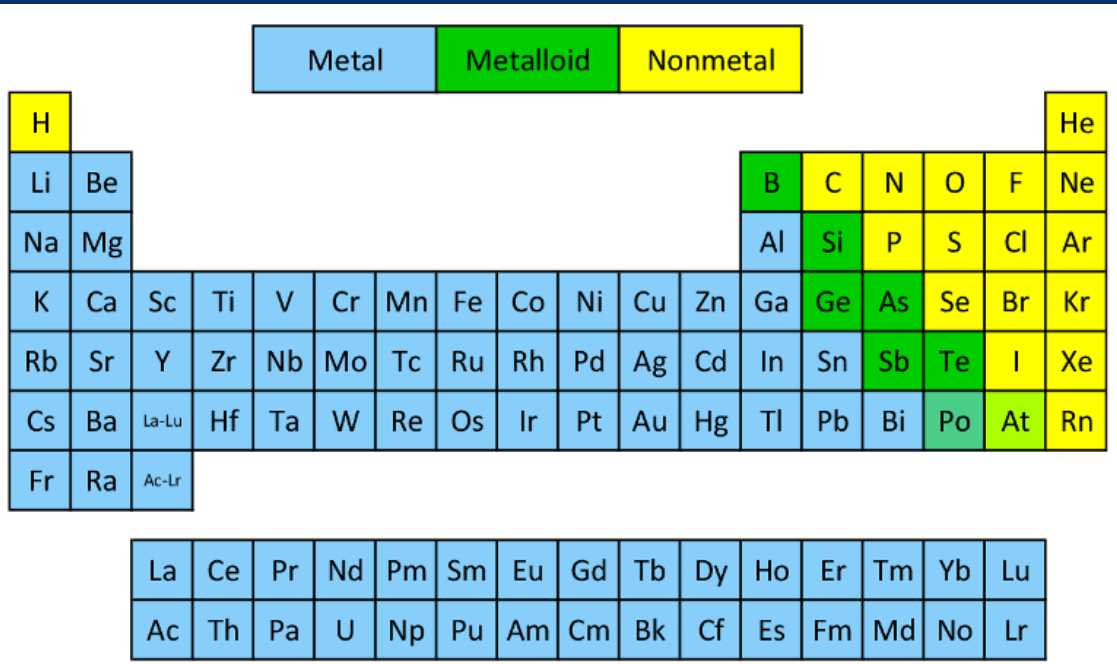
- Using the above principle, electronic configuration of elements can be decided
- Consequently the elements can be tabulated according to their electronic structure
- Such a table is called the ***periodic table***

Periodic table



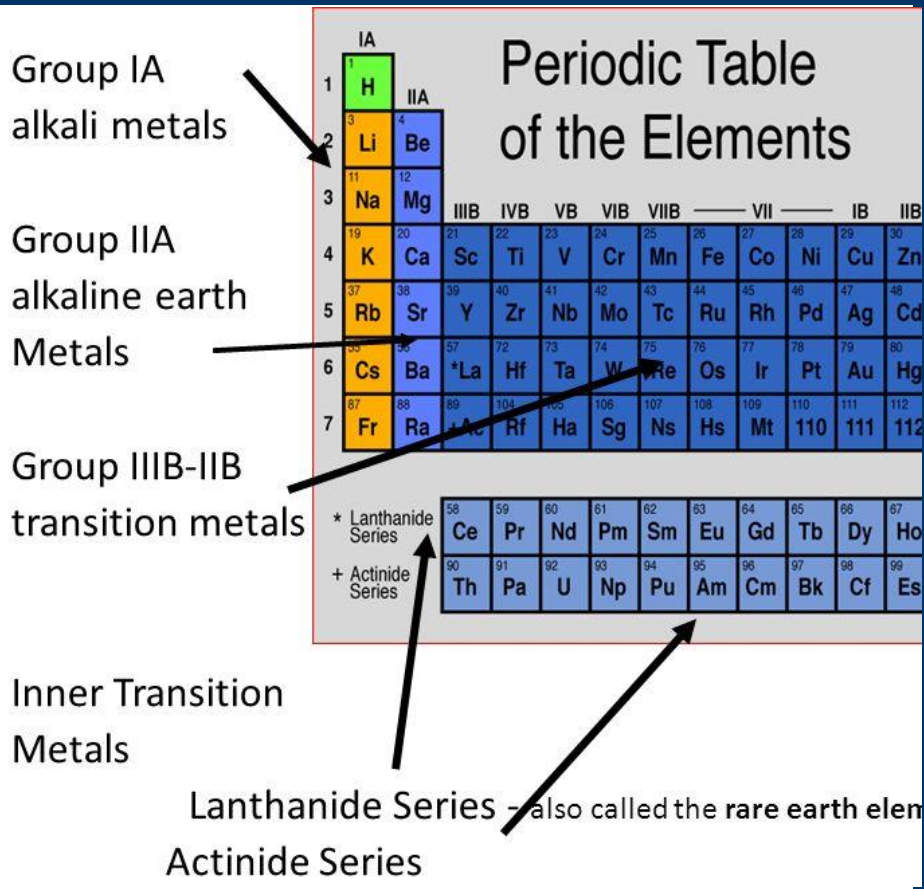


- Periodic table is arranged in the order of the atomic number.
- Rows are called ***periods*****.** Columns are called ***groups*****.**
- The elements in a row, have the same number of main energy levels



- All the elements in the periodic table can be divided into three categories:
  - Metals
  - Non – metals
  - Metalloids (elements that exhibit the properties of both metals and non – metals) – B, Si, Ge, As, Sb, Te, Po.
- About 80 % of the elements are **metals**

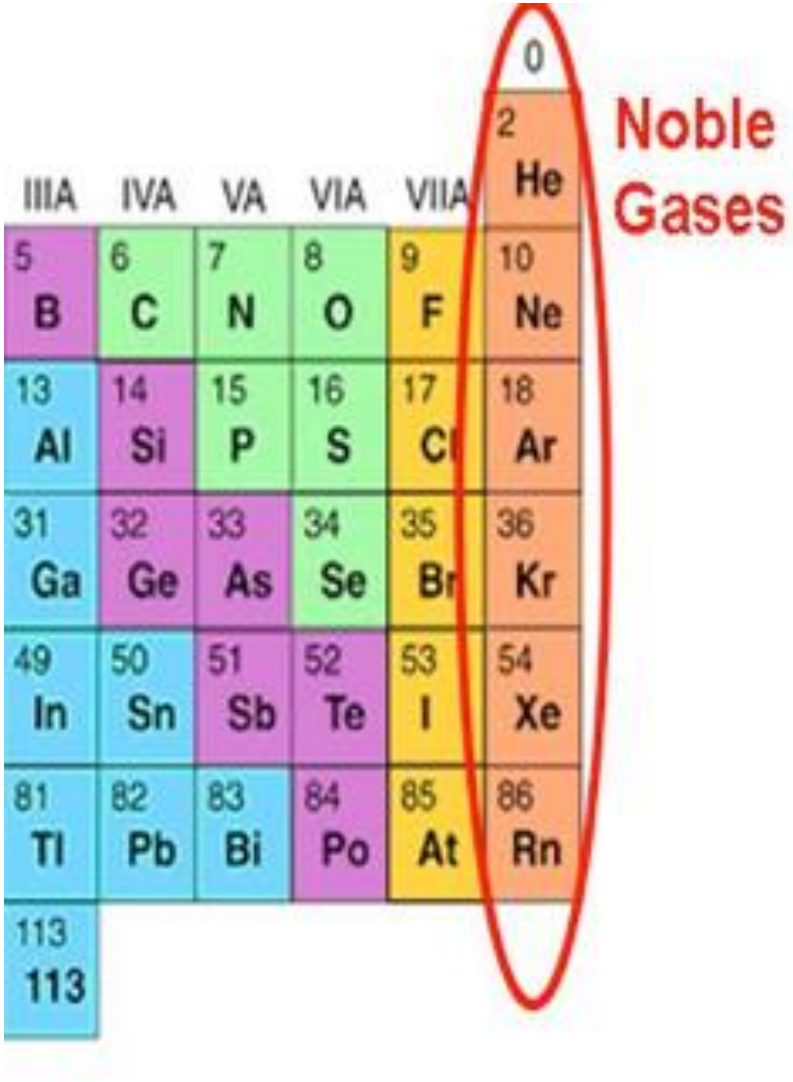
- In metals, electrons move freely from one atom to another giving high electrical and thermal conductivity, chemical reactivity etc.
- All the metals except mercury (Hg) are solid at room temperature.
- The light metals (IA & IIA) are soft and chemically reactive

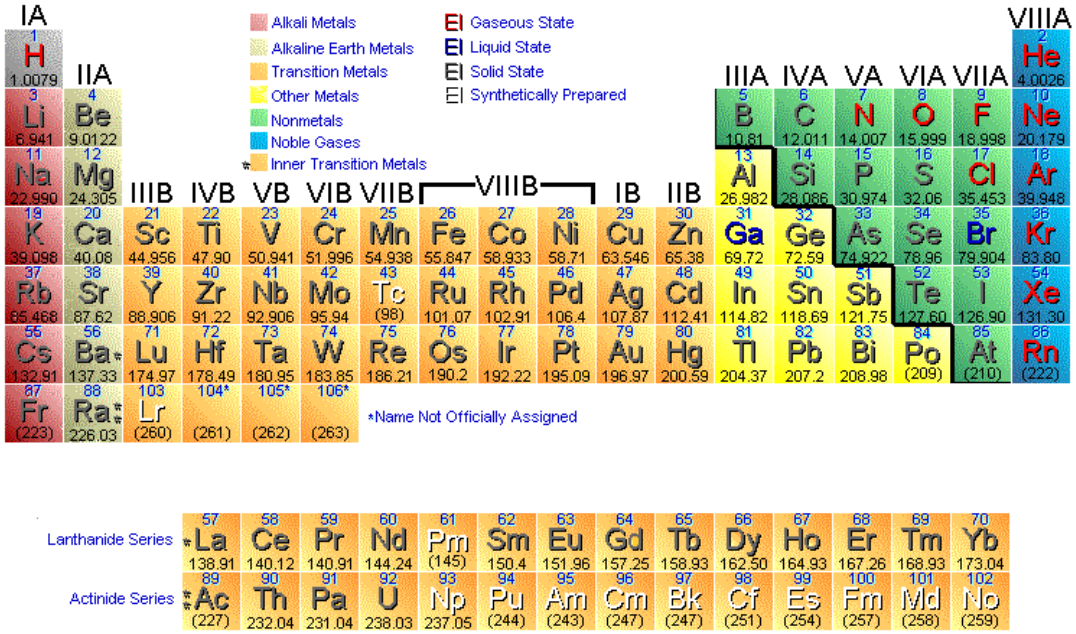


The noble gases (He, Ne, Ar, etc.,) have the last orbital fully filled and they are chemically inert or inactive.

The (groups IIIA - VIIA) have atoms in which the outermost p-orbital is filling.

Most non-metals are gaseous but bromine (Br) is a liquid.





- The (groups IB - VIIIB) are the elements in which the d-orbit is filling
- From these, the elements in which the d-orbit is not fully occupied are called the **"transition metals"** (groups IIIB – VIIIB)
- They are stronger and harder than the other metals

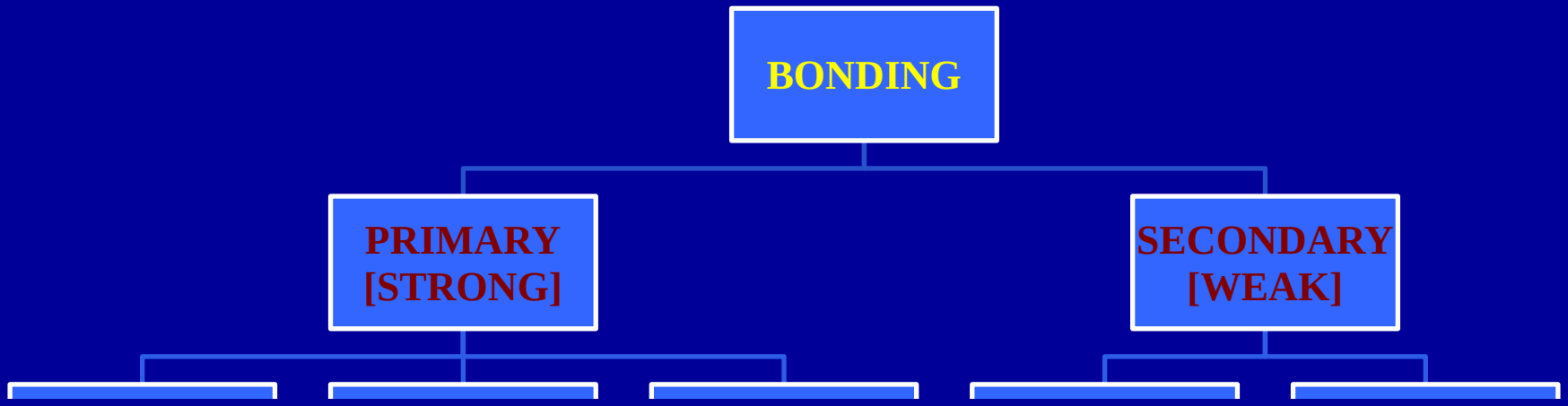
Interatomic Bonds

- Primary Bond
  - Ionic Bond
  - Covalent Bond
  - Metallic Bond
- Secondary Bond
  - Van der Waals Bond

Interatomic Bonds

- **Primary bonds** form when valence electrons are present (outer shell not completely filled)
- **Secondary bonds** form when there are no valence electrons (outer shell filled completely)

Interatomic Bonds

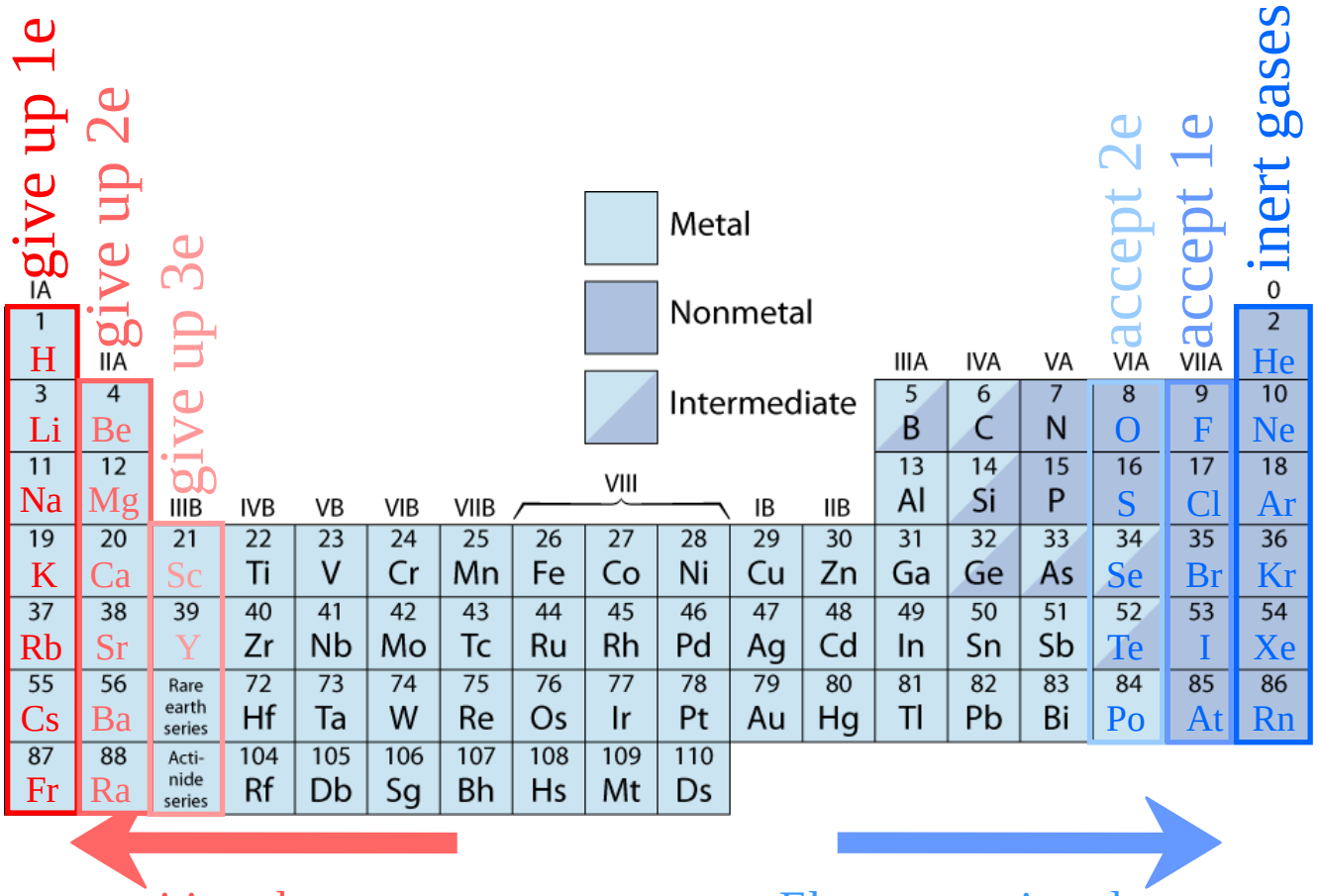


Atomic and Molecular Bonds

- **Ionic bonds :-** Strong atomic bonds due to transfer of electrons
- **Covalent bonds :-** Large interactive force due to sharing of electrons
- **Metallic bonds :-** Non-directional bonds formed by sharing of electrons
- **Permanent Dipole bonds :-** Weak intermolecular bonds due to attraction between the ends of permanent dipoles.
- **Fluctuating Dipole bonds :-** Very weak electric dipole bonds due to asymmetric distribution of electron densities.

The Periodic Table

Columns: Similar Valence Structure



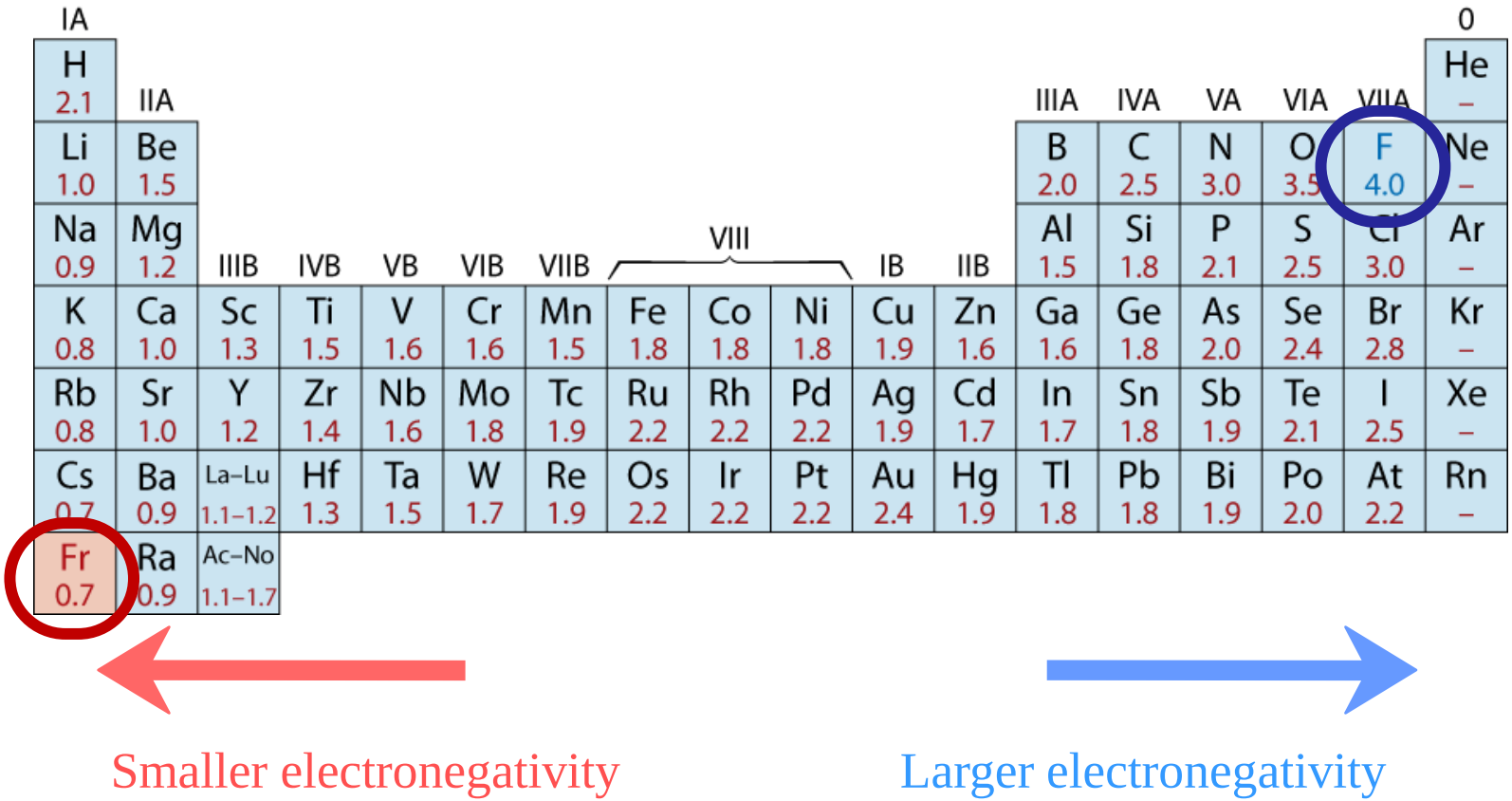
Adapted from Fig. 2.6, *Callister 7e.*

Electropositive elements: Readily give up electrons to become + ions.

Electronegative elements: Readily acquire electrons to become - ions.

Electronegativity

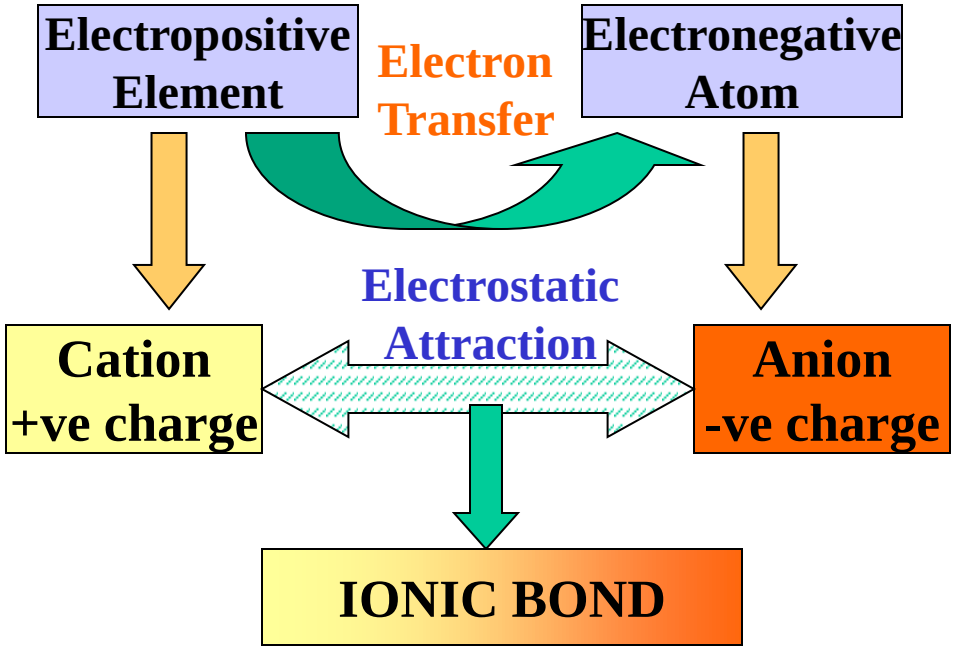
- Ranges from 0.7 to 4.0,
- Large values: tendency to acquire electrons.



Adapted from Fig. 2.7, *Callister 7e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

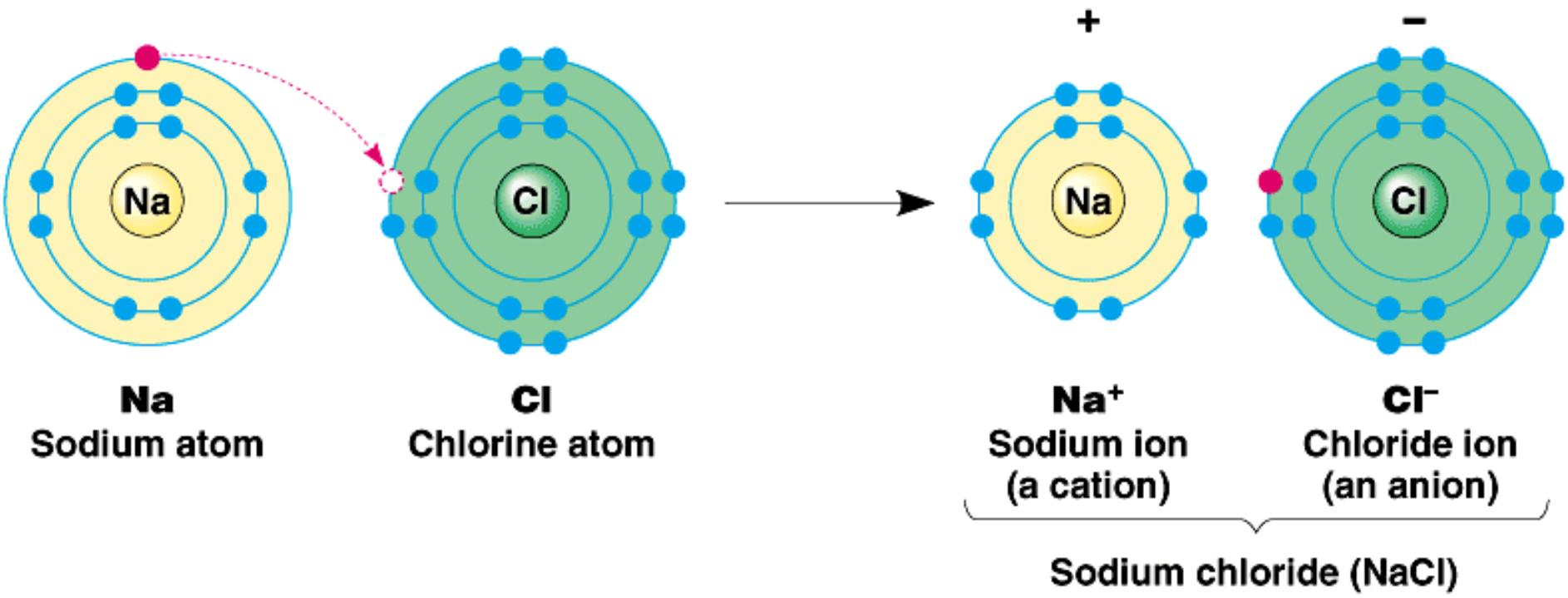
Ionic Bonding

- Ionic bonding is due to electrostatic force of attraction between cations and anions.
- It can form between metallic and nonmetallic elements.
- Electrons are transferred from electropositive to electronegative atoms.



Ionic Bonding

- Occurs between + and - ions.
- Requires electron transfer.
- Large difference in electronegativity required.
- Example: NaCl



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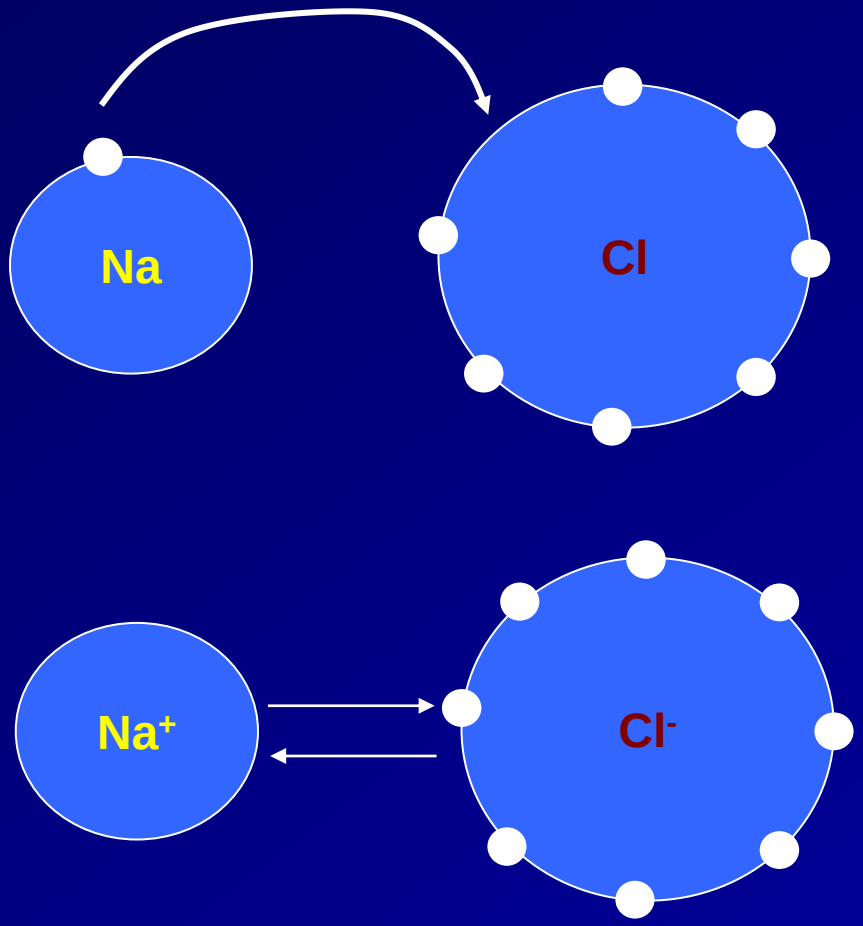
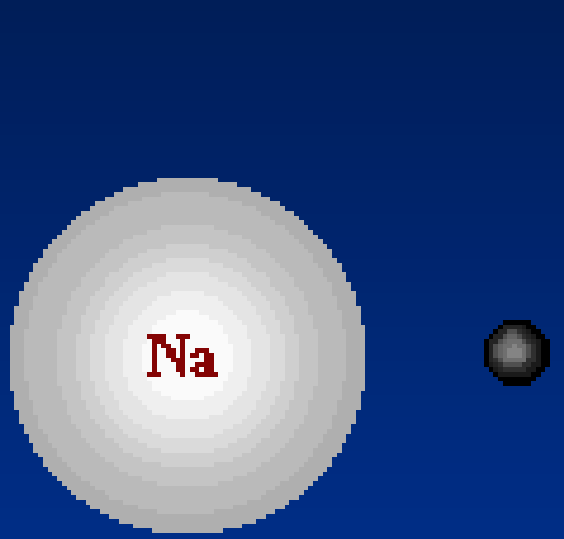
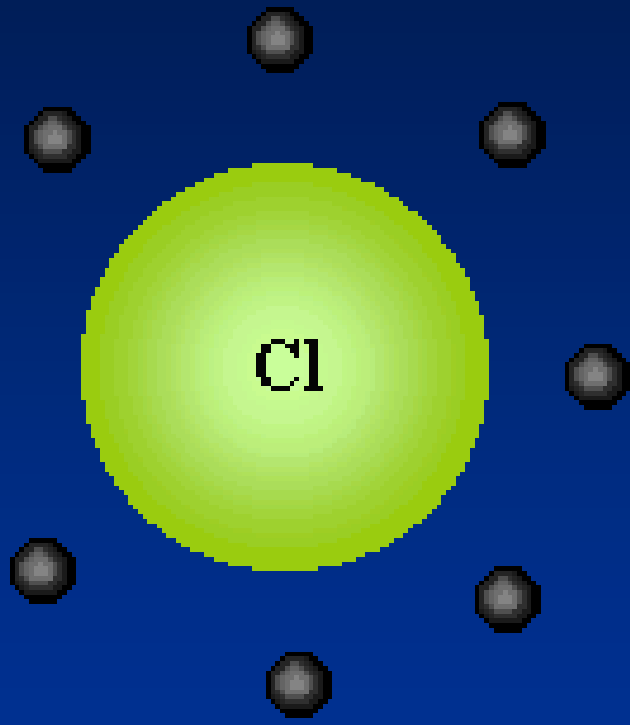
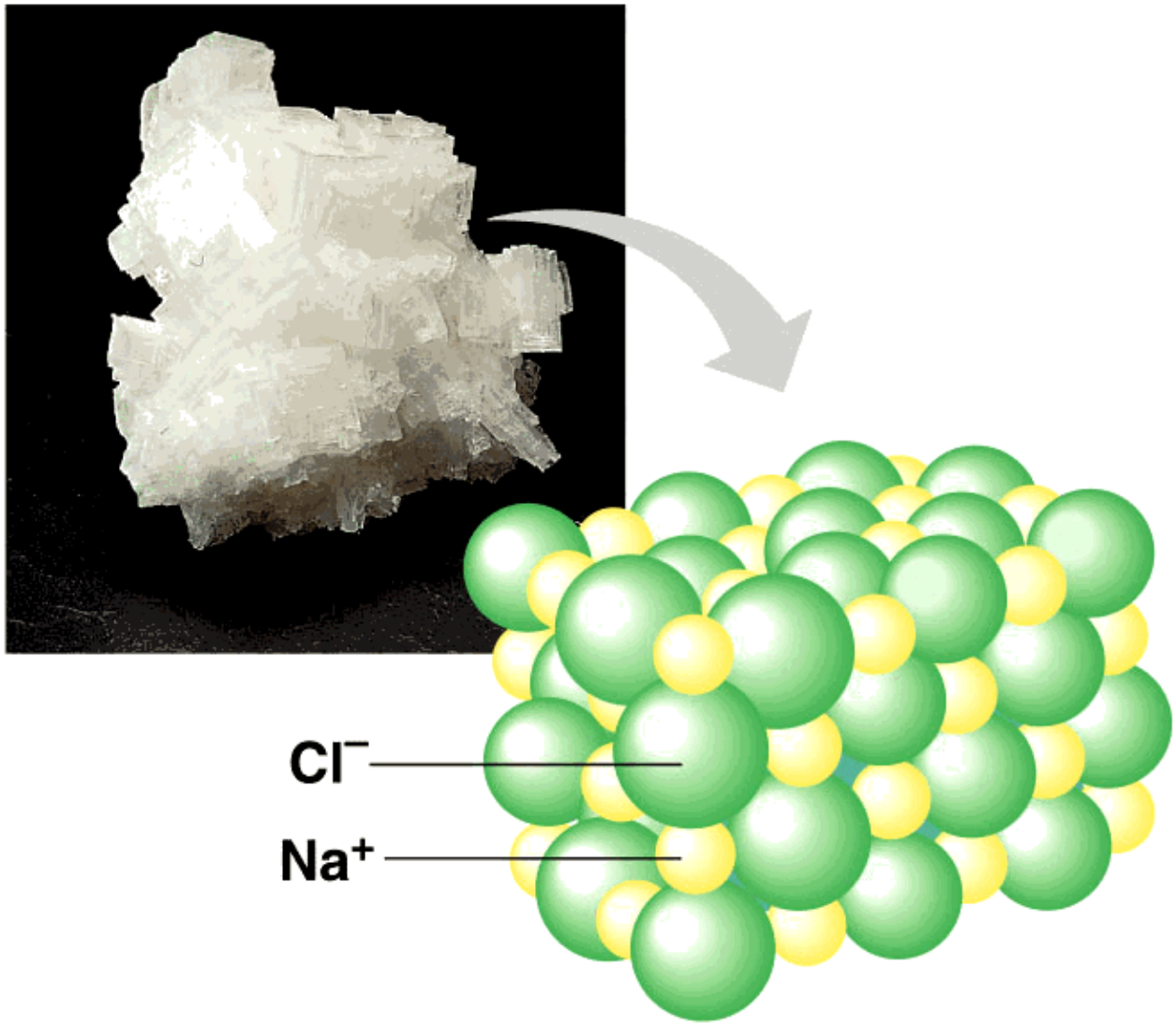
Ionic Bonding - Example




Na


Cl

Atomic arrangement – crystal structure



Ionic bond – metal + nonmetal

donates electrons

accepts electrons

Dissimilar electronegativities

ex: MgO

Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$ or [Ne] $3s^2$

O $1s^2\ 2s^2\ 2p^4$

Mg^{2+} $1s^2\ 2s^2\ 2p^6$ or [Ne]

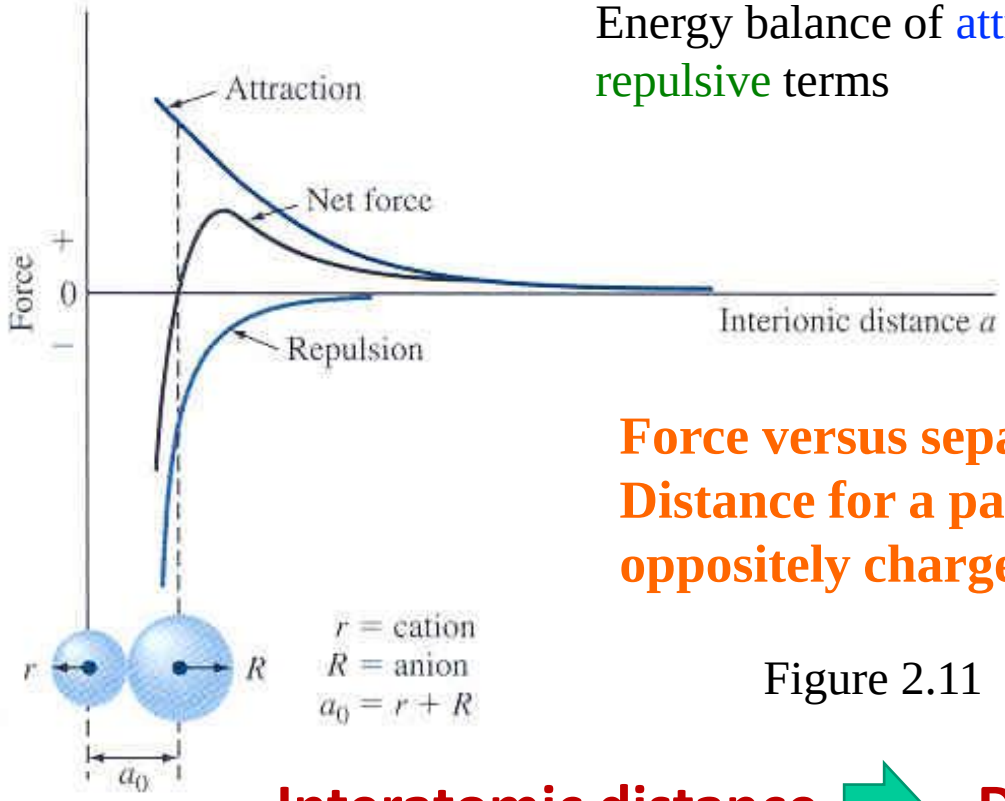
O^{2-} $1s^2\ 2s^2\ 2p^6$ or [Ne]

Ionic Force for Ion Pair

- **Nucleus of one ion attracts electron of another ion.**
- **The electron clouds of ion repulse each other when they are sufficiently close.**

Energy – minimum energy most stable

Energy balance of attractive and repulsive terms



Force versus separation Distance for a pair of oppositely charged ions

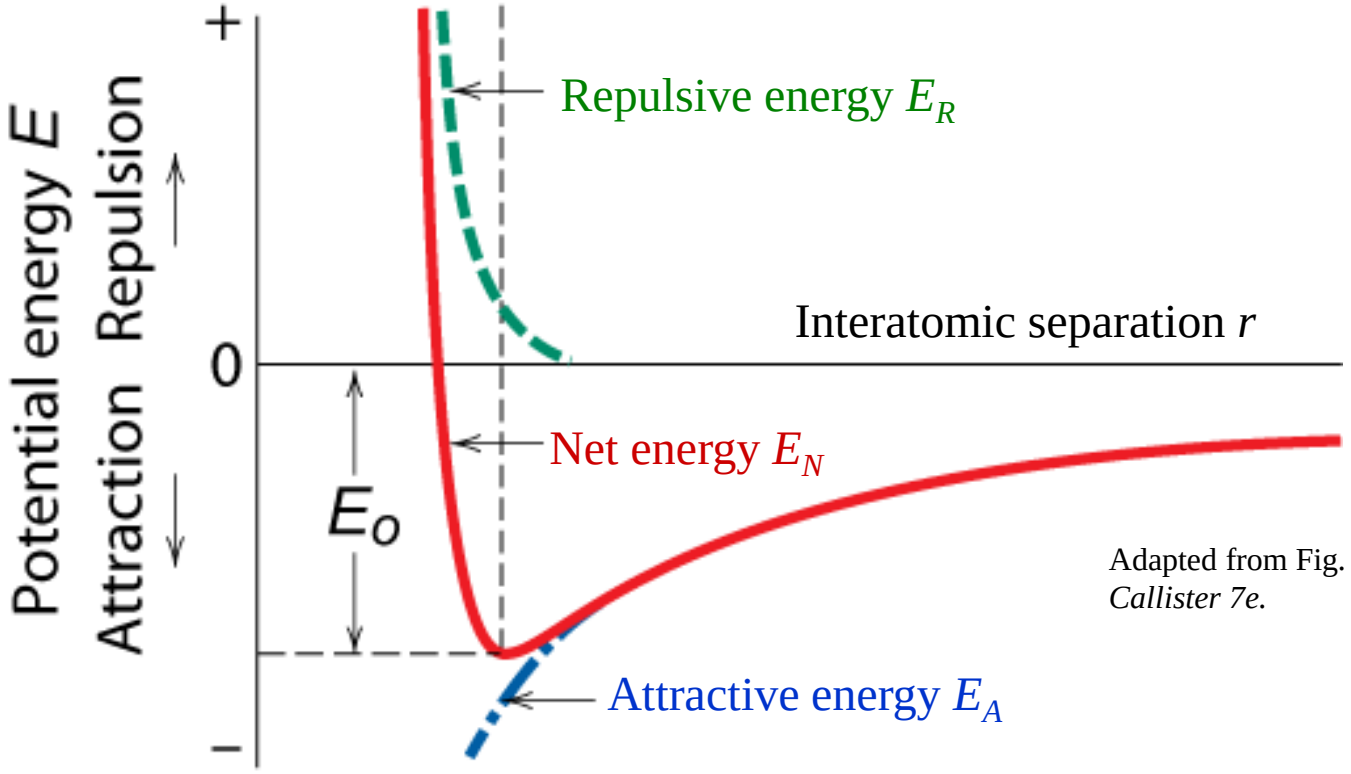
Figure 2.11

Interatomic distance ➡ **Density**

Ionic Bonding

Nucleus of one ion attracts electron of another ion.
The electron clouds of ion repulse each other when they are sufficiently close

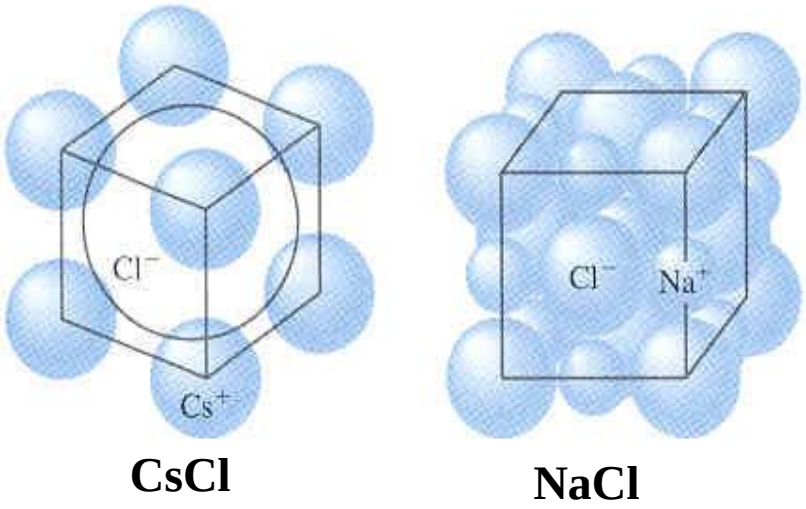
- Energy – minimum energy most stable
  - Energy balance of attractive and repulsive terms



Adapted from Fig. 2.8(b), *Callister 7e.*

Ion Arrangements in Ionic Solids

- **Ionic bonds are *Non Directional***
- **Geometric arrangements are present in solids to maintain electric neutrality.**
  - **Example:- in NaCl, six Cl- ions pack around central Na+ Ions**



CsCl **NaCl**

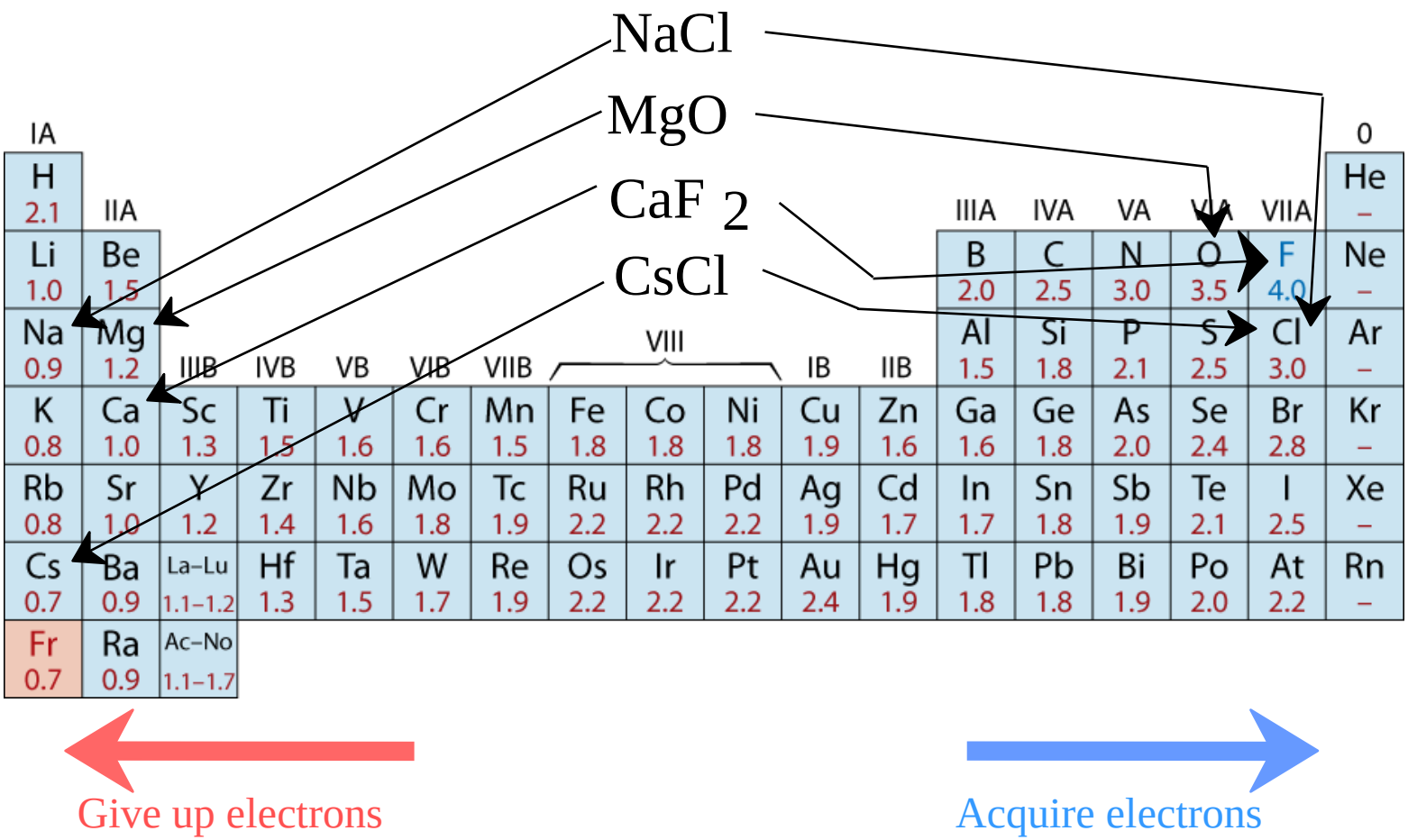
Ionic packing In NaCl and CsCl

Figure 2.13

- **As the ratio of cation to anion radius decreases, fewer anion surround central cation.**

Examples: Ionic Bonding

- Predominant bonding in Ceramics



Adapted from Fig. 2.7, *Callister 7e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

Bonding Energies

- **Lattice energies and melting points of ionically bonded solids are high.**
- **Lattice energy decreases when size of ion increases.**
- **Multiple bonding electrons increase lattice energy.**

➢ **Example :-**

NaCl	**Lattice energy = 766 kJ/mol**
	Melting point = 801 ^{o}C
CsCl	**Lattice energy = 649 kJ/mol**
	Melting Point = 646 ^{o}C
BaO	**Lattice energy = 3127 kJ/mol**
	Melting point = 1923 ^{o}C

METALLIC BOND

- Metallic bond forms in metals
- It is an arrangement of positive ion cores in a 'sea' of electrons
- Electrons that form this electron sea are 'free' to move within the structure and thus known as *free electrons*
- These free electrons make the metals good conductors of electricity and heat

Metallic Bonding

- **Atoms in metals are closely packed in crystal structure.**
- **Loosely bonded valence electrons are attracted towards nucleus of other atoms.**
- **Electrons spread out among atoms forming electron clouds.**
- **These free electrons are reason for electric conductivity and ductility**
- **Since outer electrons are shared by many atoms, metallic bonds are *Non-directional***

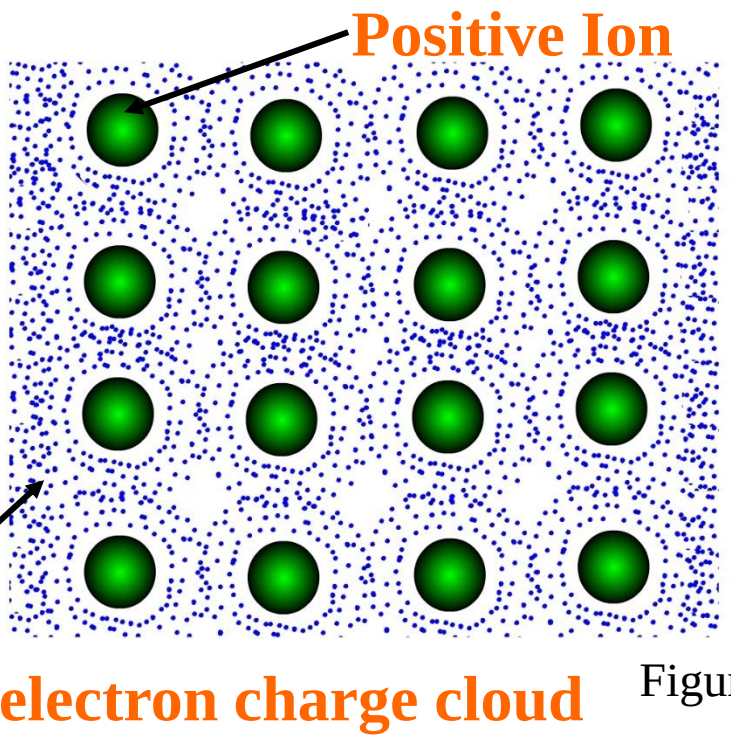
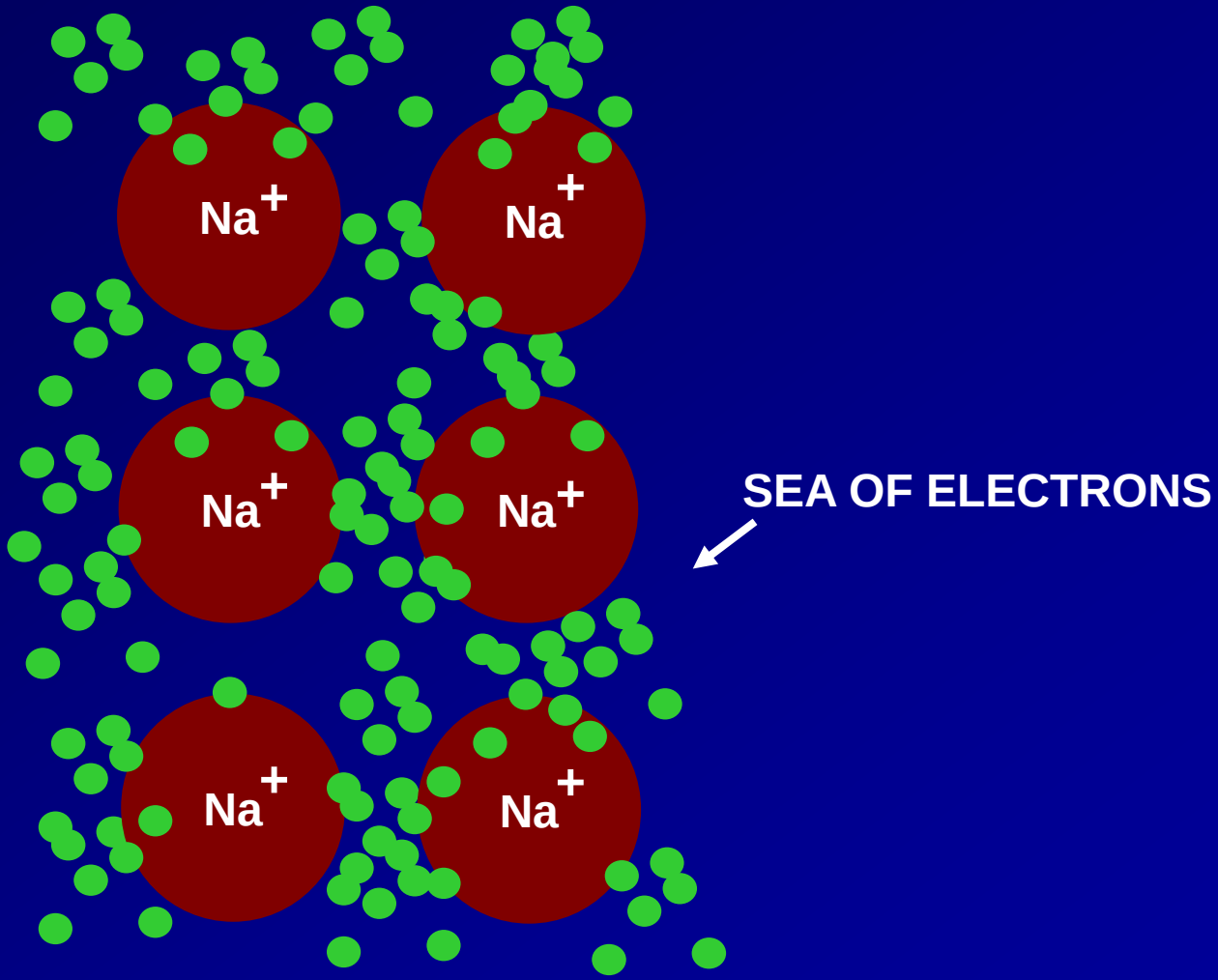


Figure 2.24


Na+
Na+
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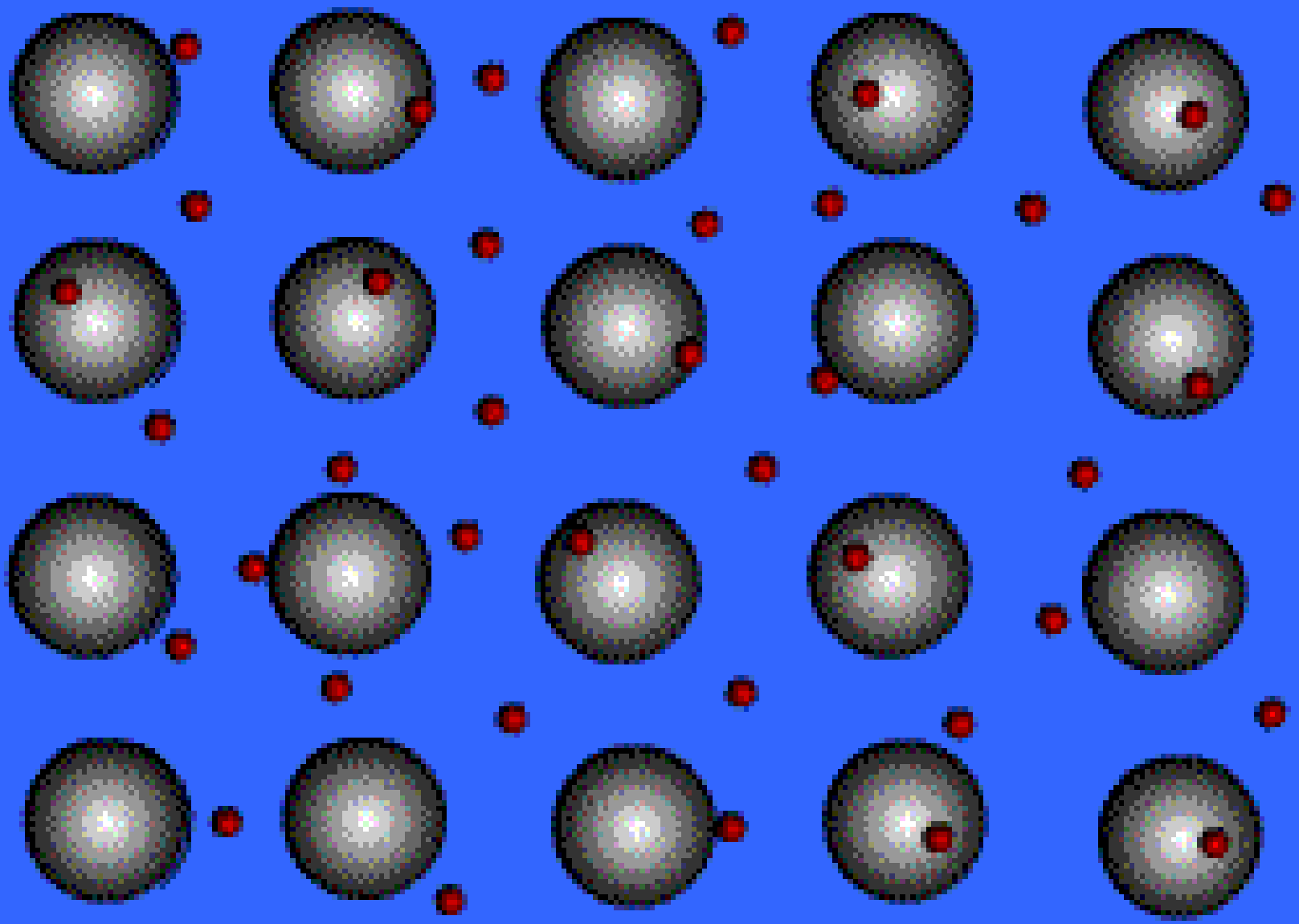
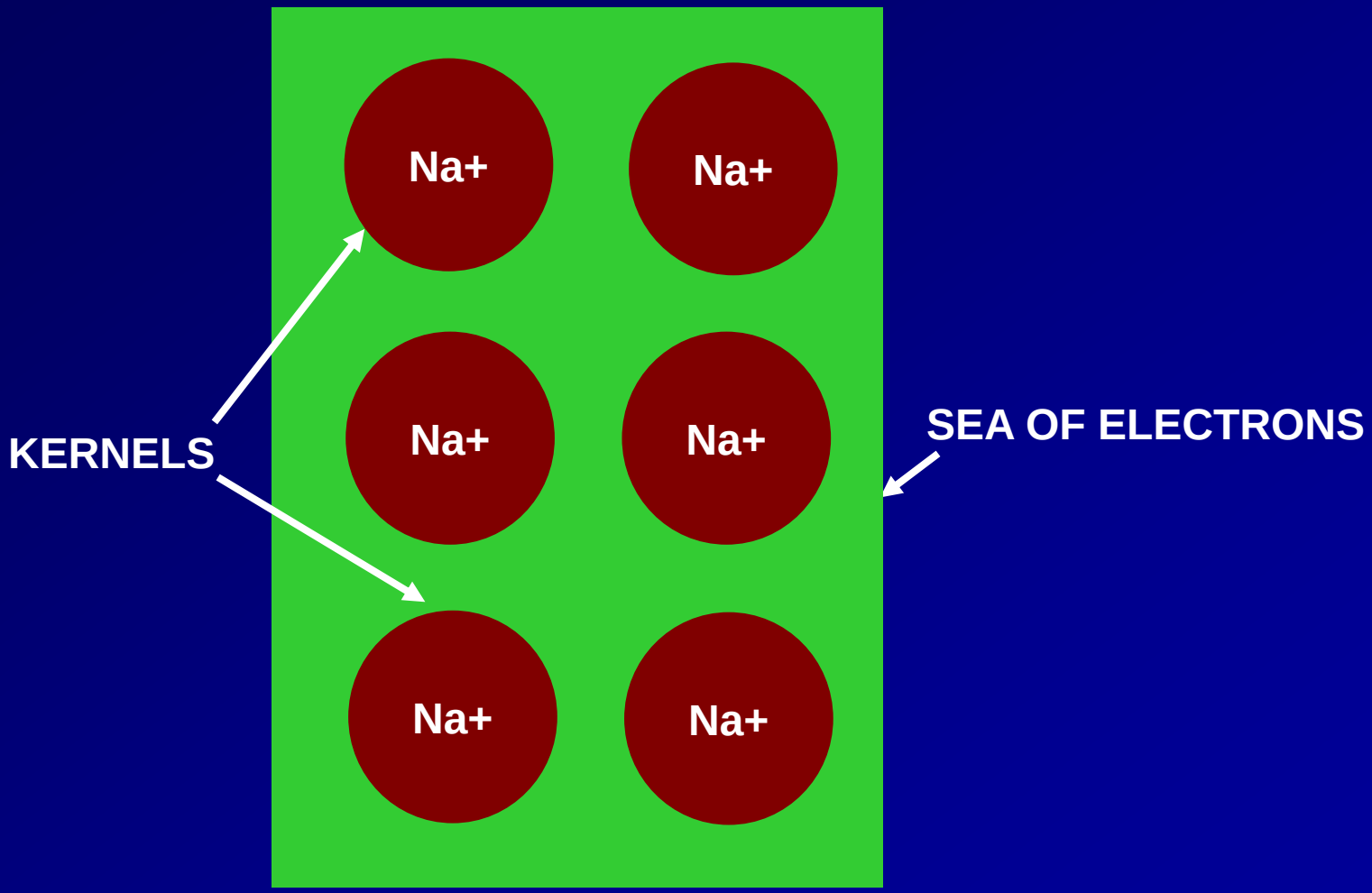
Na+
SEA OF ELECTRONS



Kernels

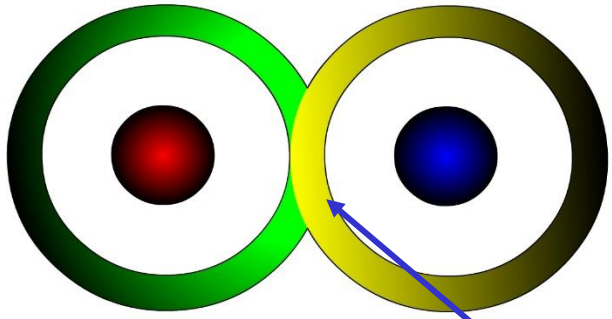

Na+
Na+
Na+
Na+
Na+
Na+
KERNELS
SEA OF ELECTRONS

Metallic Bonds (Cont..)

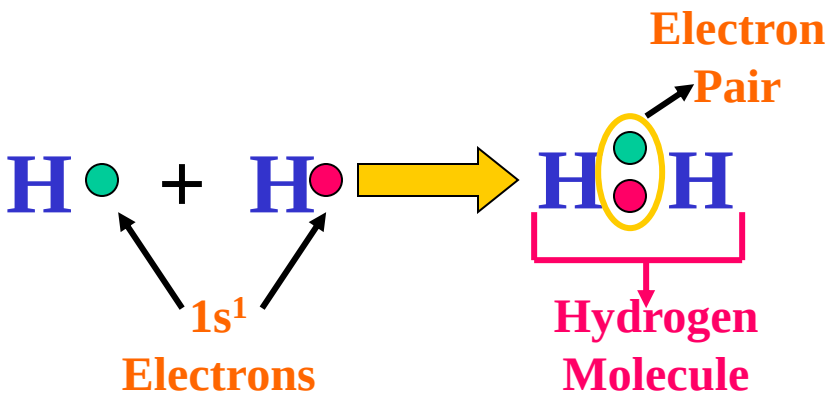
- **Overall energy of individual atoms are lowered by metallic bonds**
- **Minimum energy between atoms exist at equilibrium distance a_0**
- **Fewer the number of valence electrons involved, more metallic the bond is.**
  - **Example:-** **Na** → **Bonding energy 108 kJ/mol, Melting temperature 97.7 °C**
- **Higher the number of valence electrons involved, higher is the bonding energy.**
  - **Example:-** **Ca** → **Bonding energy 177 kJ/mol, Melting temperature 851 °C**

Covalent Bonding

- **In Covalent bonding, outer s and p electrons are shared between two atoms to obtain noble gas configuration.**
- **Takes place between elements with small differences in *electronegativity* and close by in periodic table.**
- **In Hydrogen, a bond is formed bet sharing their $1s^1$ electrons**



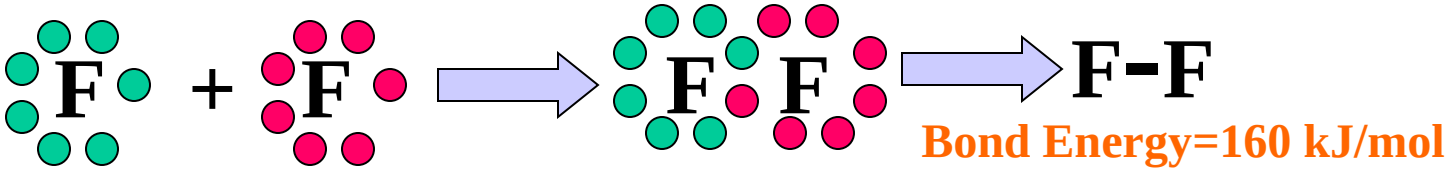
Overlapping Electron Clouds



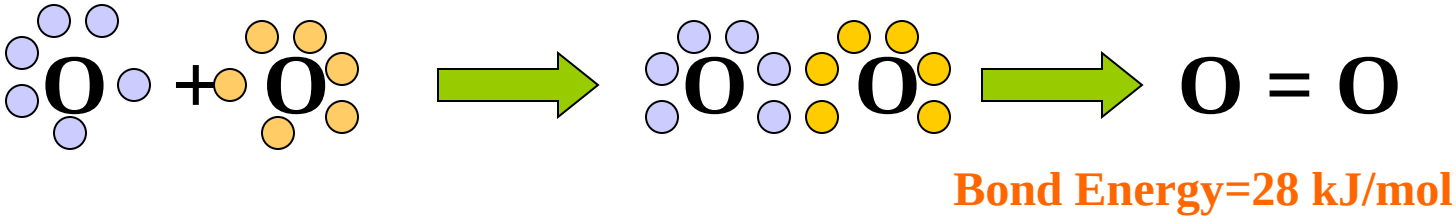
Covalent Bonding

Covalent Bonding - Examples

- **In case of F_2, O_2 and N_2, covalent bonding is formed by sharing p electrons**
- **Fluorine gas (Outer orbital – $2s^2\ 2p^5$) share one p electron to attain noble gas configuration.**



- **Oxygen (Outer orbital - $2s^2\ 2p^4$) atoms share two p electrons**



- **Nitrogen (Outer orbital - $2s^2\ 2p^3$) atoms share three p electrons**

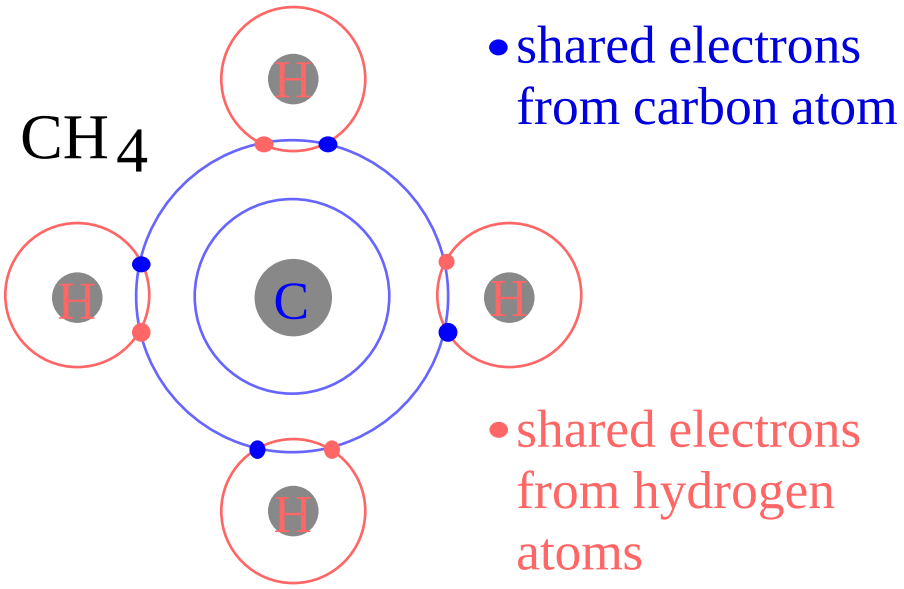
Covalent Bonding

- similar electronegativity ∴ share electrons
- bonds determined by valence – *s* & *p* orbitals dominate bonding
- Example: CH_4

C: has 4 valence e^-, needs 4 more

H: has 1 valence e^-, needs 1 more

Electronegativities are comparable.



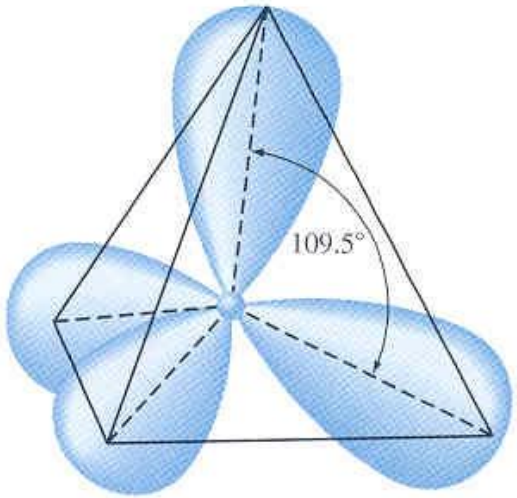
Adapted from Fig. 2.10, *Callister 7e.*

H_2

H_2O

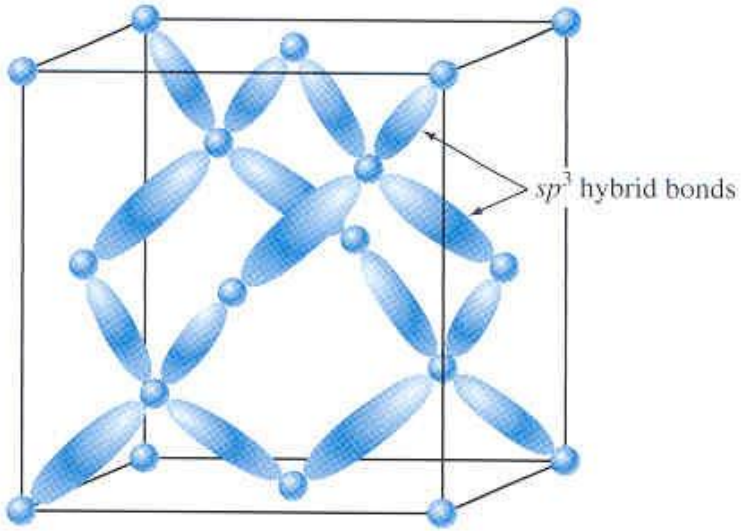
Structure of Diamond

- **Four sp^3 orbitals are directed *symmetrically* toward corners of regular tetrahedron.**
- **This structure gives high hardness, high bonding strength (711 kJ/mol) and high melting temperature (3550 °C).**



Carbon Atom

Figure 2.18

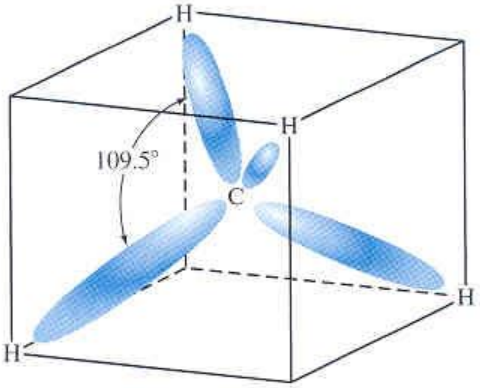


Tetrahedral arrangement in diamond

Figure 2.19

Carbon Containing Molecules

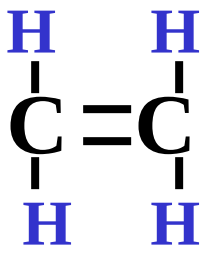
- **In Methane, Carbon forms four covalent bonds with Hydrogen.**
- **Molecules are very weakly bonded together resulting in low melting temperature (-183°C).**



Methane molecule

Figure 2.20

- **Carbon also forms bonds with itself.**
- **Molecules with multiple carbon bonds are more reactive.**
  - **Examples:-**

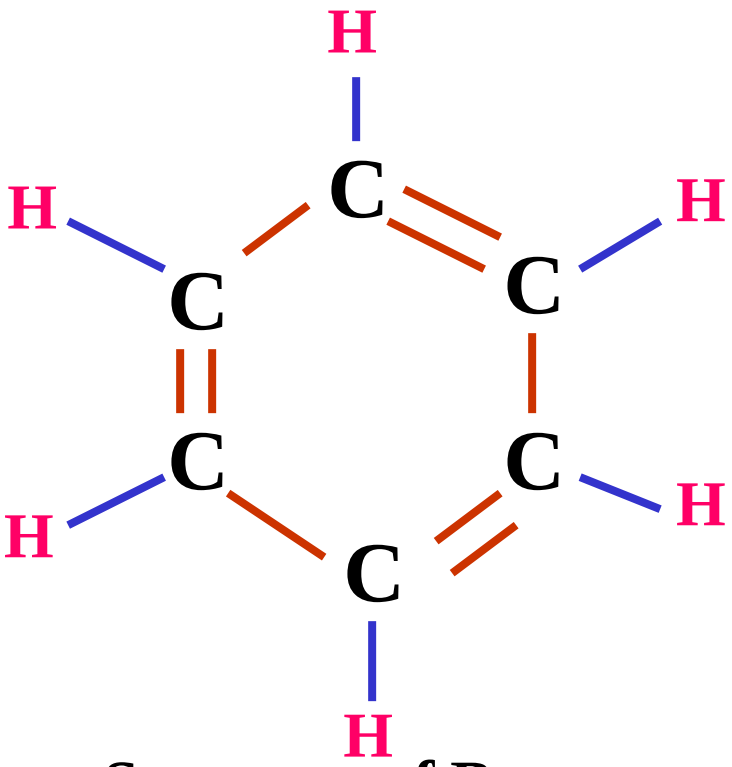


Ethylene

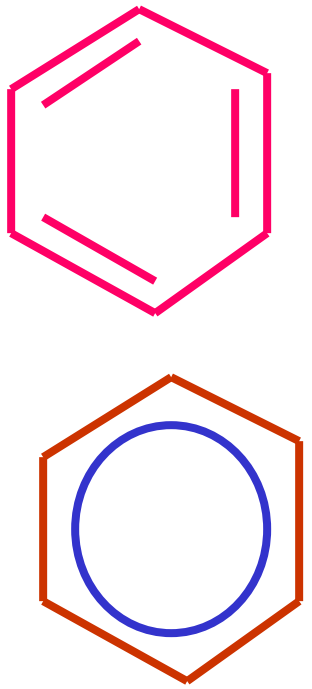
Acetylene

Covalent Bonding in Benzene

- **Chemical composition of Benzene is C_6H_6.**
- **The Carbon atoms are arranged in hexagonal ring.**
- **Single and double bonds alternate between the atoms.**



Structure of Benzene



Simplified Notations

Figure 2.23

SECONDARY BONDING

- **Secondary bonds are due to attractions of *electric dipoles* in atoms or molecules.**
- **Dipoles are created when positive and negative charge centers exist.**

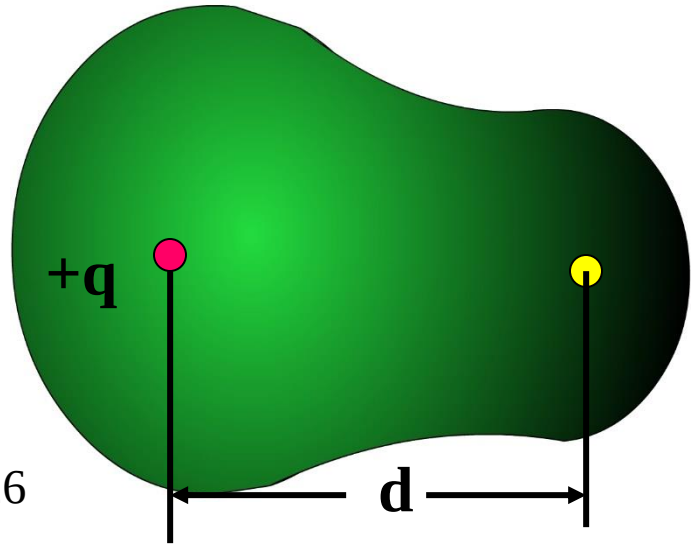


Figure 2.26

Dipole moment=μ =q.d

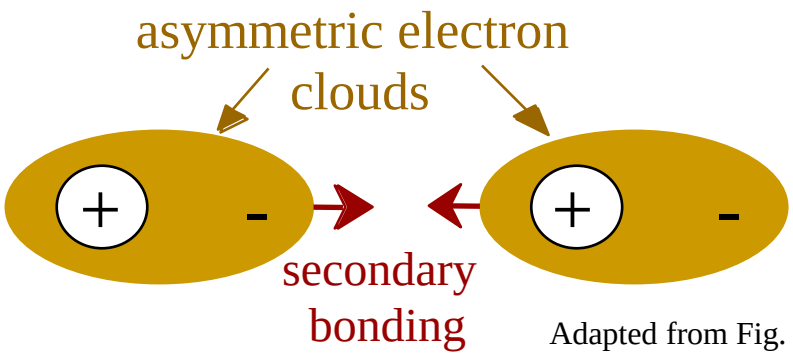
q= Electric charge
d = separation distance

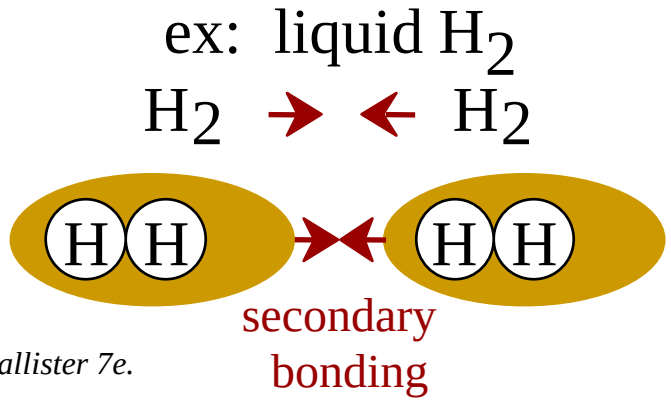
- **There two types of bonds ➡ permanent and fluctuating.**

SECONDARY BONDING

Arises from interaction between dipoles

- Fluctuating dipoles





Adapted from Fig. 2.13, *Callister 7e.*

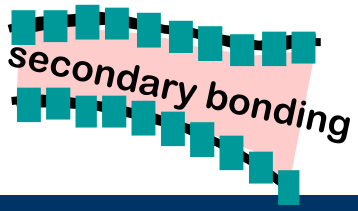
- Permanent dipoles-molecule induced

-general case:

Adapted from Fig. 2.14, *Callister 7e.*

-ex: liquid HCl

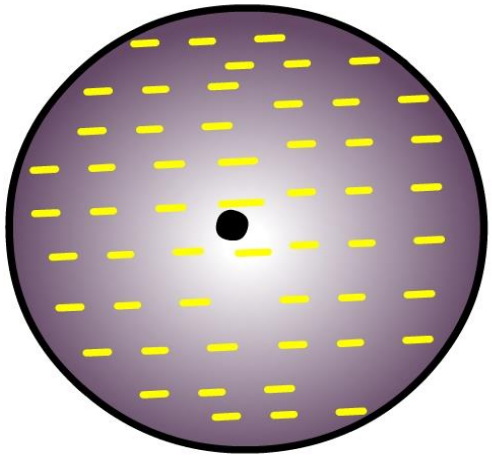
-ex: polymer



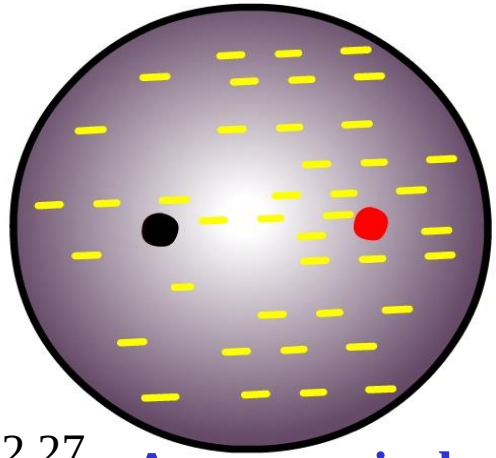
secondary bonding

Fluctuating Dipoles

- **Weak secondary bonds in noble gasses.**
- **Dipoles are created due to asymmetrical distribution of electron charges.**
- **Electron cloud charge changes with time.**



Symmetrical distribution of electron charge



Asymmetrical Distribution (Changes with time)

Figure 2.27

Permanent Dipoles

- **Dipoles that do not fluctuate with time are called Permanent dipoles.**

➢ **Examples:-**

CH_4 → **Symmetrical Arrangement Of 4 C-H bonds** → **No Dipole moment**

CH_3Cl → **Asymmetrical Tetrahedral arrangement** → **Creates Dipole**

Hydrogen Bonds

- **Hydrogen bonds are *Dipole-Dipole interaction* between polar bonds containing hydrogen atom.**

  ➢ **Example :-**

  - ❖ **In water, dipole is created due to asymmetrical arrangement of hydrogen atoms.**
  - ❖ **Attraction between positive oxygen pole and negative hydrogen pole.**

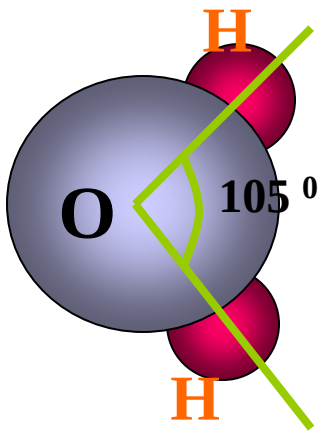
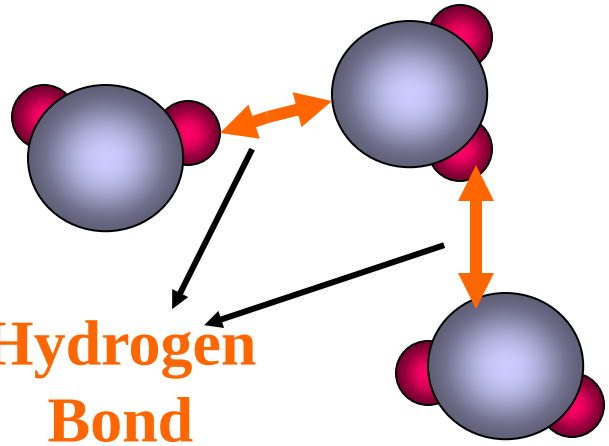


Figure 2.28

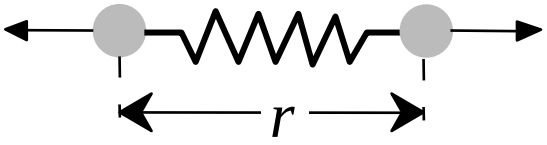


Summary: Bonding

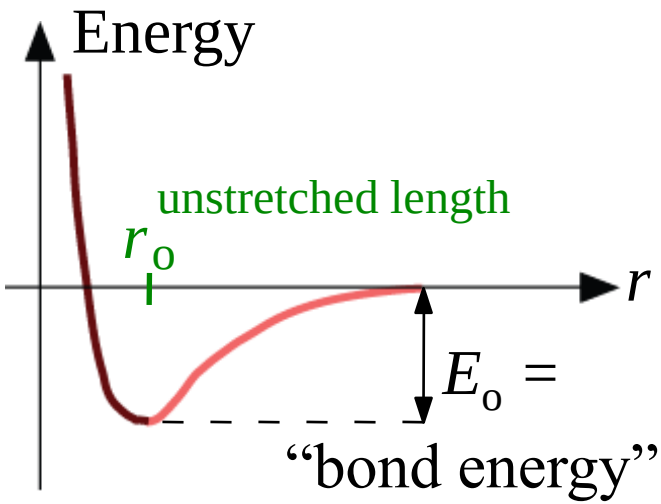
Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional (semiconductors, ceramics polymer chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular

Properties From Bonding: T_m

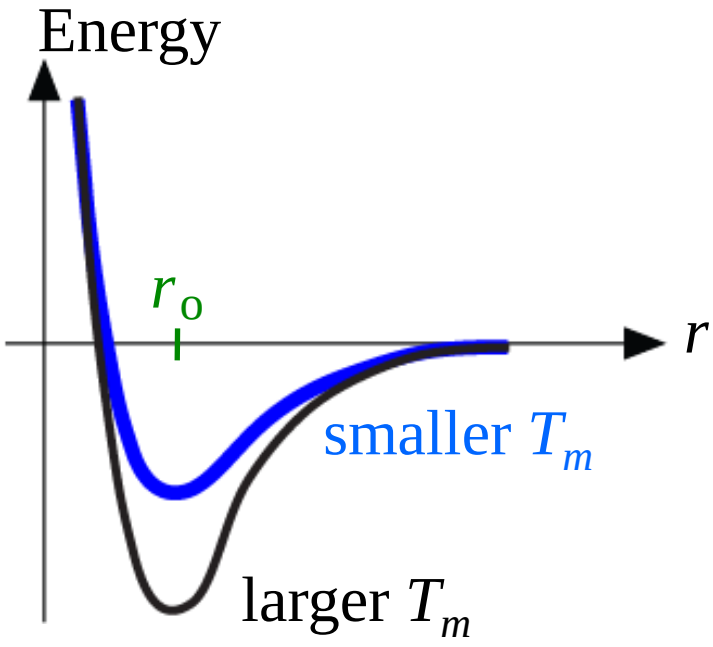
- Bond length, r



- Bond energy, E_o



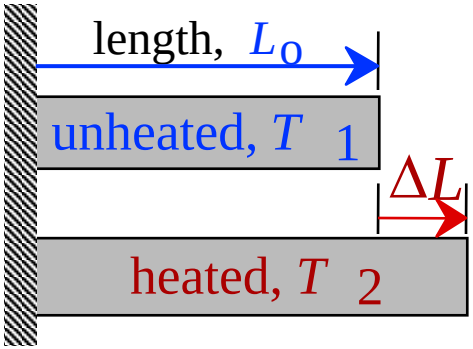
- Melting Temperature, T_m



T_m is larger if E_o is larger.

Properties From Bonding : α

- Coefficient of thermal expansion, α

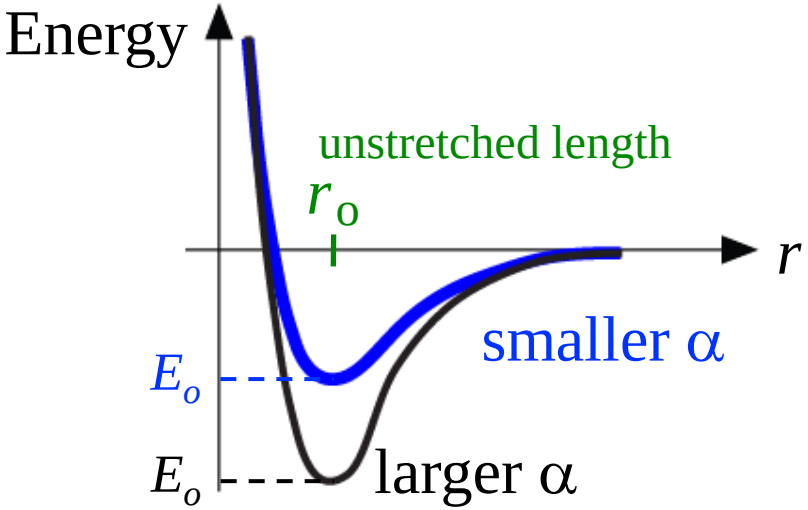


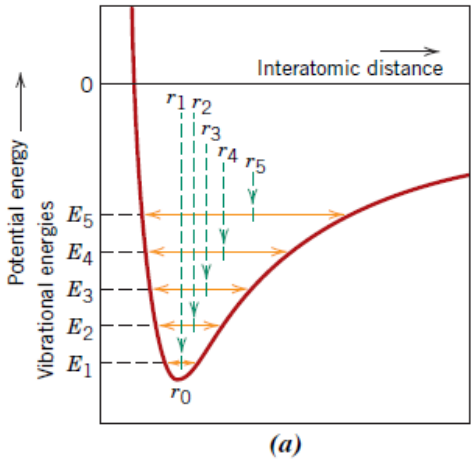
coeff. thermal expansion

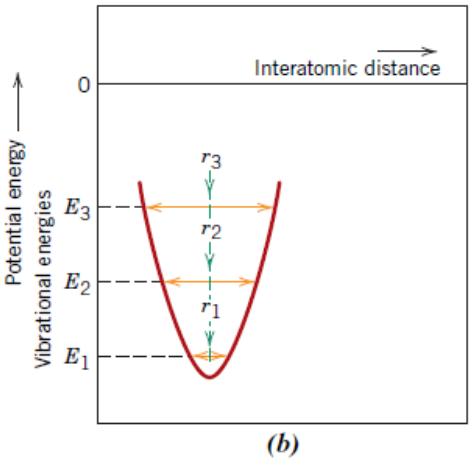
$$\frac{\Delta L}{L_o} = \alpha\,(T_2 - T_1)$$

- α ~ symmetry at r_o

α is larger if E_o is smaller.

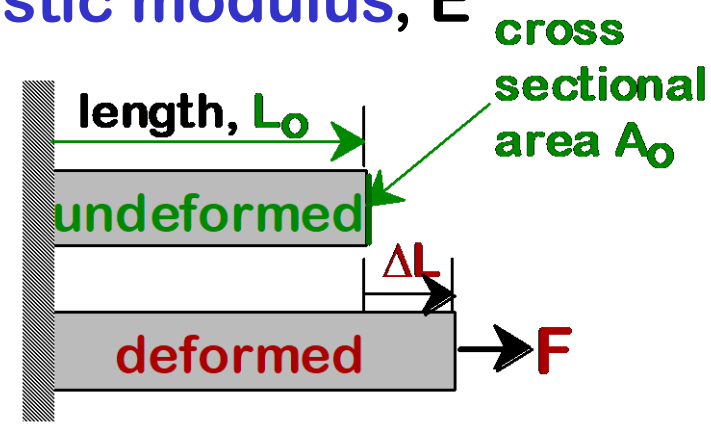






PROPERTIES FROM BONDING: E

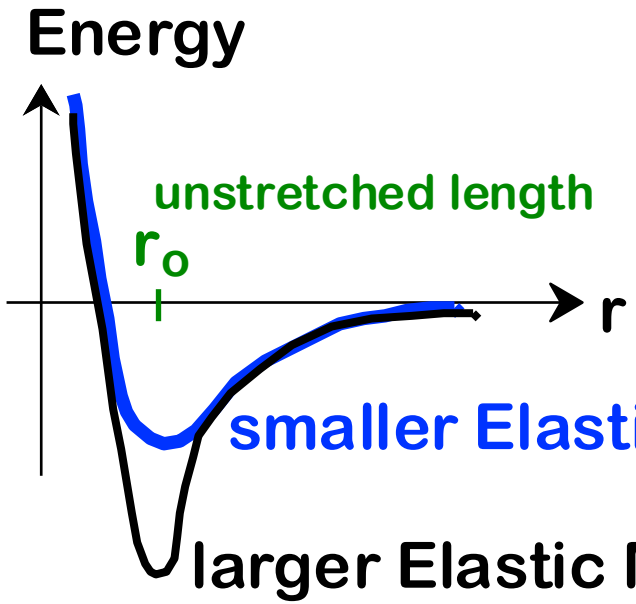
- **Elastic modulus, E**



Elastic modulus

$$\frac{F}{A_o} = E\frac{\Delta L}{L_o}$$

- **E ~ curvature at r_o**



E is larger if E_o is larger.

Summary: Primary Bonds

Ceramics

(Ionic & covalent bonding):

Large bond energy

large T_m
large E
small α

Metals

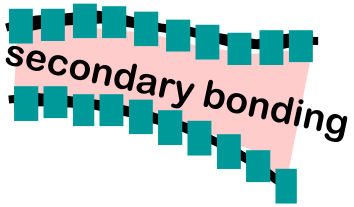
(Metallic bonding):

Variable bond energy

moderate T_m
moderate E
moderate α

Polymers

(Covalent & Secondary):



Directional Properties

Secondary bonding dominates

small T_m
small E
large α